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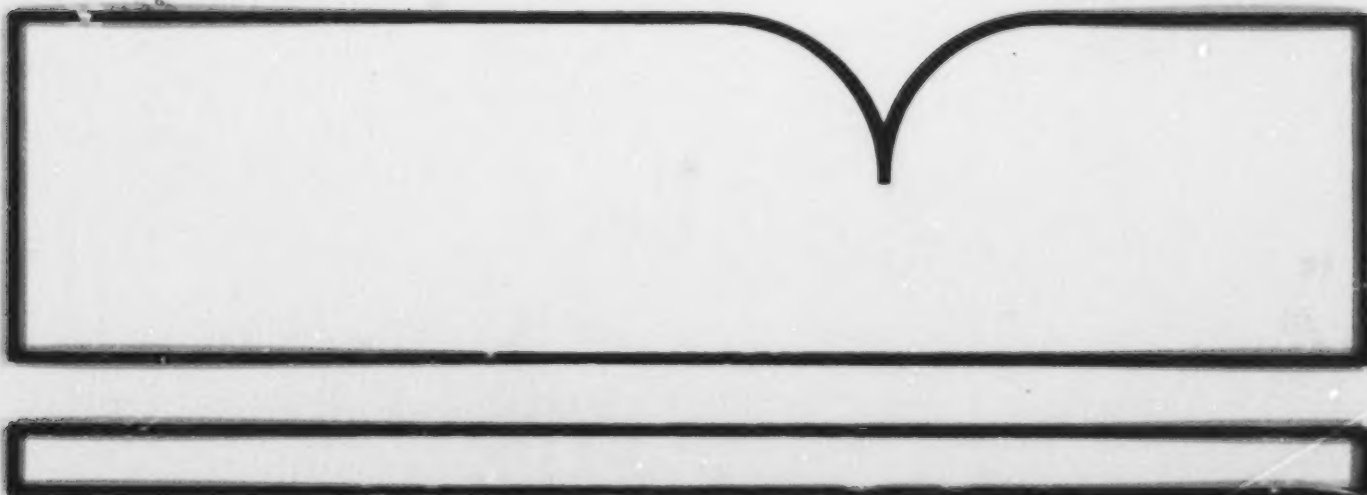
Continuous Performance Monitoring Techniques for  
Hazardous Waste Incinerators

Energy and Environmental Research Corp., Irvine, CA

Prepared for:

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CONTINUOUS PERFORMANCE MONITORING TECHNIQUES  
FOR HAZARDOUS WASTE INCINERATORS

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| 16. ABSTRACT<br>The report describes a study to determine the feasibility of utilizing real-time continuous exhaust measurements of combustion intermediates as a way to monitor incinerator performance. The key issue was to determine if a direct correlation exists between destruction efficiency (DE) and intermediate species concentration measurements. Two general correlations were observed: (1) the correlation between DE, THC, and CH <sub>4</sub> is nearly proportional, and (2) the CO correlation indicates that a significant increase in CO emissions is necessary before the exhaust concentration of waste compounds increases substantially. Study data support several conclusions, including: (1) a turbulent spray flame operating without afterburners or postflame gas cleaning can achieve a DE of >99.99%; (2) flame conditions that minimize CO, THC, and CH <sub>4</sub> emissions result in optimum waste DE; (3) less-than-optimum DE was accompanied by increased release of intermediate species; (4) the range of conditions for optimum flame performance (defined by CO, THC, and CH <sub>4</sub> ) was found to be $\leq$ the range for high DE; and (5) CO increased significantly under some conditions in which the DE remained high. |                                                                                                                                                         |                                                |
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## 1.0 INTRODUCTION

A number of programs sponsored by the U.S. Environmental Protection Agency have shown that thermal destruction is an effective technique for eliminating organic hazardous waste. Both field testing of operating incinerators (Trenholm et al., 1983) and bench scale testing on turbulent diffusion spray flames (Seeker et al., 1983) have indicated that properly operated incinerators are very efficient. They have been found to destroy compounds to typically greater than 99.99 percent destruction and removal efficiency (DRE) when operated correctly. However, there is currently no methodology for continuously monitoring the performance of the hazardous waste incinerator.

There are presently over 300 organic wastes identified by the EPA as being hazardous (40 CFR part 261, Appendix VIII). A particular waste stream may consist of a number of these compounds and assurance must be given that the incinerator is not releasing any of them during normal operation. Because of the wide range of compounds and the low concentration levels that need to be measured, direct real-time continuous monitoring is beyond the state-of-the-art of measuring techniques. The EPA licensing procedure requires that high efficiency operation (DRE > 99.99 percent) be demonstrated prior to operation for a selected set of constituents in the waste stream. After licensing, the incinerator is maintained within the range of operating conditions stipulated in the permit. During routine operation, it is desirable to monitor the destruction efficiency of the unit and thereby allow corrective action to be initiated at the onset of unsafe performance. Methods available to measure specific hazardous waste compounds that are used during licensing trial burns (e.g., organic trapping and gas chromatography separation and analysis) are unsuitable for routine performance monitoring. They are both skill- and labor-intensive, noncontinuous, and the results are not immediately available after sampling.

Thus, there is a need for development of an indirect real-time continuous monitoring methodology for hazardous waste incinerator performance. A number of indirect methodologies have been proposed. For the purposes of the current discussion, the potential methodologies can be grouped into the following general categories:

- Tracer measurements (within waste stream composition or added).
- System parameter measurements (pressure, temperature, flow rate).
- Combustion intermediate species measurements (e.g., CO, hydrocarbons).
- Combustion product measurements ( $\text{CO}_2$ ,  $\text{O}_2$ ,  $\text{NO}_x$ ).

Methodologies which rely on these measurements are largely untested and not completely developed. This study will concentrate on the use of intermediate species as a measure of incinerator performance since they appear most feasible at this time. Field tested and relatively low cost instrumentation is commercially available for several of the stable species.

The combustion of organic molecules is a complex series of elementary reaction steps involving a myriad of intermediate species. For example, to completely describe the oxidation of the simplest organic, methane, requires more than 100 reactions and involves 25 intermediate species. For more complex organics, the numbers increase geometrically with the molecular weight. However, only a few of the species are stable. These include the following:

- Lower molecular weight hydrocarbons
- Methane
- Carbon monoxide
- Formaldehyde

Also, these stable intermediates are common to the combustion of most organic compounds including hazardous waste and auxiliary fuels.

Organics burn in a complex series of fundamental reaction steps that eventually leads through CO as the principal intermediate before the complete oxidized state ( $\text{CO}_2$ ) is reached. Carbon monoxide is a thermally stable compound in comparison to hazardous waste organics. Since it is an intermediate, large amounts of CO are produced in the flame zone that will be eventually destroyed if mixing is good. If mixing is poor, CO can escape the flame by mechanisms of thermal quenching. Excessive carbon monoxide emissions usually reflect poor mixing or incorrectly set combustion air. The CO

level measured in the stack depends on many factors, including waste properties, spray nozzle design and operation, combustion air mixing pattern, and incinerator chamber design. Carbon monoxide can be continuously measured using nondispersive infrared analyzers to levels down to a few ppm concentration.

Exhaust emissions of hydrocarbons arise from three sources: (1) the unburned hazardous organic constituents due to a low destruction efficiency, (2) unburned hydrocarbons from the auxiliary fuel, and (3) intermediate hydrocarbons generated during the combustion of the hazardous waste and auxiliary fuel. Which of these is the dominant source depends on the operating condition of the incinerator. However, the dominant source is likely the intermediate and, in particular, the light intermediates such as methane that are typically more thermally stable than the hazardous and fuel constituents. Total hydrocarbons can be measured with flame ionization detector (FID) instrumentation down to a few ppm, while methane can be measured with similar sensitivity using a nondispersive infrared analyzer (NDIR). Formaldehyde is another hydrocarbon intermediate but is somewhat less stable than CO or CH<sub>4</sub> and no suitable instrumentation is currently available for routine continuous monitoring.

The objective of this study is to determine the feasibility of an incinerator performance monitoring methodology based upon real-time continuous exhaust measurements of combustion intermediates, specifically: carbon monoxide, total hydrocarbons, and methane. The key issue is what kind of correlation exists between DRE and these intermediate species. The approach to the study encompassed the following five steps:

1. A review of methods for monitoring of intermediate species in exhaust gases.
2. A selection of instruments for evaluation.
3. An evaluation of the instruments for response and potential interferences.
4. An experiment in which a set of test organic compounds are incinerated in a laboratory-scale turbulent diffusion spray flame.

5. An analysis of the exhaust gas for both destruction efficiency of the waste compounds and the emission of intermediate species over a range of operating conditions from high- to low-efficiency operation.

This approach was designed to determine if any correlation exists between the level of combustion intermediates and the destruction efficiency in the turbulent spray flame. The turbulent flame reactor (TFR) can be operated under conditions where destruction efficiencies (DE)\* are very high (>99.999 percent). The test conditions investigated were selected to cover a range of low-efficiency conditions as well in which four modes of failure were allowed to occur:

- Fuel rich
- Excessively fuel lean
- Poor atomization quality
- Flame quench

These failure modes were selected as being representative of poor operation conditions that might exist for liquid injection incinerators.

The exhaust concentrations of the test hazardous waste compounds were measured along with the concentrations of total hydrocarbons, CH<sub>4</sub>, and CO for each of the conditions delineated above in order to assess the correspondence between DE and the concentration of intermediate species. The test compounds were mixed to three percent by mass with diesel fuel and introduced to the reactor. The compounds used--acrylonitrile, benzene, chloroform, and chlorobenzene--were selected because they are all EPA-listed hazardous organic compounds and because they are expected to represent a broad range of incinerability behavior (Kramlich et al., 1983).

Quality Assurance/Quality Control requirements are applicable to this project. The data contained in this report are NOT supported by QA/QC documentation as required by the United States Environmental Protection Agency's Quality Assurance Policy.

\*In this report a distinction is drawn between waste destruction efficiency (DE) and waste destruction and removal efficiency (DRE). DE is based on measurement of input and output concentrations of a specific species across a thermal treatment reactor but upstream of any control device which removes that species from the flow exhaust.

## 2.0 EXPERIMENTAL

This section includes a review of the available continuous monitoring techniques, the reasons for selecting certain continuous monitors, and descriptions of the turbulent flame reactor, the sampling and analytical systems, and the laboratory facility.

### 2.1 Review of Continuous Monitoring Techniques

The techniques available for continuous monitoring of combustion intermediates vary for the species to be measured. Compounds likely to be present in an exhaust stream are unburned fuel, combustion products such as  $H_2O$  and  $CO_2$ , and intermediates such as  $CO$ ,  $CH_4$ , and  $CH_2O$ , and other hydrocarbons. Unburned fuel and intermediates are of major importance because their concentrations in an exhaust stream will increase during upset conditions. Instruments are currently available for specifically measuring  $CO$  and  $CH_4$ . Instrumentation equipped with a Flame-Ionization Detector is also available for measuring total hydrocarbons. Thus, the species chosen for possible monitoring are  $CO$ ,  $CH_4$ , and total hydrocarbons. The techniques available for continuous measurement of these species include flame ionization, nondispersive infrared, automated gas chromatography and photoionization (Seeker et al., 1981).

Flame ionization is based on the formation of ions when hydrocarbons are directed into hydrogen-air or hydrogen-oxygen flame. A Flame-Ionization Detector (FID) is used to detect the extent of ionization and responds to nearly all hydrocarbons in the exhaust stream, thus giving a direct indication of unburned hydrocarbons in the stack gas. However, the FID sensitivity is dependent on the specific hydrocarbon in the exhaust, as will be demonstrated. Nondispersive Infrared (NDIR) utilizes the IR absorption properties of a specific species. The gas of interest, say  $CO$ , is trapped on both sides of a flexible diaphragm in an enclosed detector housing. Radiation from two nondispersive infrared sources is directed through separate tubes, one directed to one side of the detector, and the second directed to the other side of the detector. One tube, called the reference cell, is permanently filled with a nonabsorbing background gas, usually nitrogen. The sample stream is conveyed through the other tube. If the gas of interest,  $CO$  in this case, is present in the sample stream, some of the radiation will be

absorbed in the sample tube resulting in a reduction in the amount of radiation that arrives at the sample tube side of the detector. In addition to CO, methane (CH<sub>4</sub>) is also amenable to NDIR detection.

Automated gas chromatography (GC) can be used to determine the total Gaseous Nonmethane Organics (TGNMO). The sample gas is conditioned, transported to and analyzed by a semiportable GC equipped with an FID. The TGNMO fraction is separated from other constituents by using various GC columns, oxidized to CO<sub>2</sub>, and then reduced to CH<sub>4</sub> before it is introduced to the FID. The system is automated, but not continuous, and requires the attention of a skilled operator.

The Photo-Ionization Detector (PID) is similar to an FID except that a UV radiation source is used to induce ionization. If the ionization potential of the compound is less than the UV lamp energy, then the detector will respond to that compound. Use of this method requires a lamp energy selection that will maximize the analytical visibility of the important intermediates while avoiding irrelevant background compounds. Also, the relative sensitivity of the compound in question must be determined.

## 2.2 Instrument Selection

The instruments evaluated in the present study were selected according to the following criteria:

1. The method must monitor the species previously mentioned which are likely related to destruction efficiency.
2. The method must be sensitive enough to detect species concentrations in the range required to ensure a specified destruction efficiency.
3. The method must be continuous.
4. The method should be suitable for field use; i.e., relatively easy to operate and reliable.
5. The method must be accurate.
6. The method must be free from interferences which cannot be compensated for.

7. The method must be commercially available.

The instrument selected for measuring CO is the Anarad Model AR-500R NDIR analyzer. An NDIR analyzer (Beckman Model 864) was also chosen for the continuous measurement of CH<sub>4</sub>. For THC, an FID analyzer (Beckman 402) was used. The photoionization detector was not evaluated as a result of the expense and relative complexity. TGNMO was not selected for similar reasons in addition to the failure to provide a continuous measurement.

Two of the selected instruments are designed to monitor specific compounds (CH<sub>4</sub> and CO) and one instrument monitors a class of compounds (THC). For each instrument, the response to the compounds of interest must be determined and possible interferences noted. For instance, the hydrocarbon analyzer does not give the same response to all hydrocarbons, but gives approximately twice the signal for the same concentration of ethane as methane. The response is generally accepted to be related to carbon number. Hydrocarbons other than CH<sub>4</sub> are also known to give a response with the CH<sub>4</sub> NDIR analyzer because of a strong tendency for hydrocarbons to absorb IR radiation over a very broad range of wavelengths. In contrast to the FID, however, the response of the CH<sub>4</sub> NDIR analyzer to CH<sub>4</sub> is dominant. It is also known that CO<sub>2</sub> can give a response on a CO NDIR analyzer. Thus, a series of tests were performed at the outset to determine the response of the three analyzers to compounds that are typical of exhaust products: CO, CO<sub>2</sub>, CH<sub>4</sub>, C<sub>2</sub>H<sub>2</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>6</sub>, and C<sub>3</sub>H<sub>8</sub>.

A check-out test was first performed to confirm linear response of the hydrocarbon and CH<sub>4</sub> analyzers to CH<sub>4</sub>. Various concentrations of CH<sub>4</sub> in air were made in an 11-liter mixing chamber ranging from 23 ppm to 1000 ppm. A second linearity check was performed by delivering 995 ppm CH<sub>4</sub> in air and N<sub>2</sub> from pressurized cylinders through calibrated rotameters to produce CH<sub>4</sub> concentrations ranging from 50 to 500 ppm. The results of these tests are shown in Figure 2-1. Both instruments are shown to respond linearly to CH<sub>4</sub>. With this information, it was confirmed that these instruments could be calibrated with CH<sub>4</sub> span gas of concentration ranging from 100 to 1000 ppm.

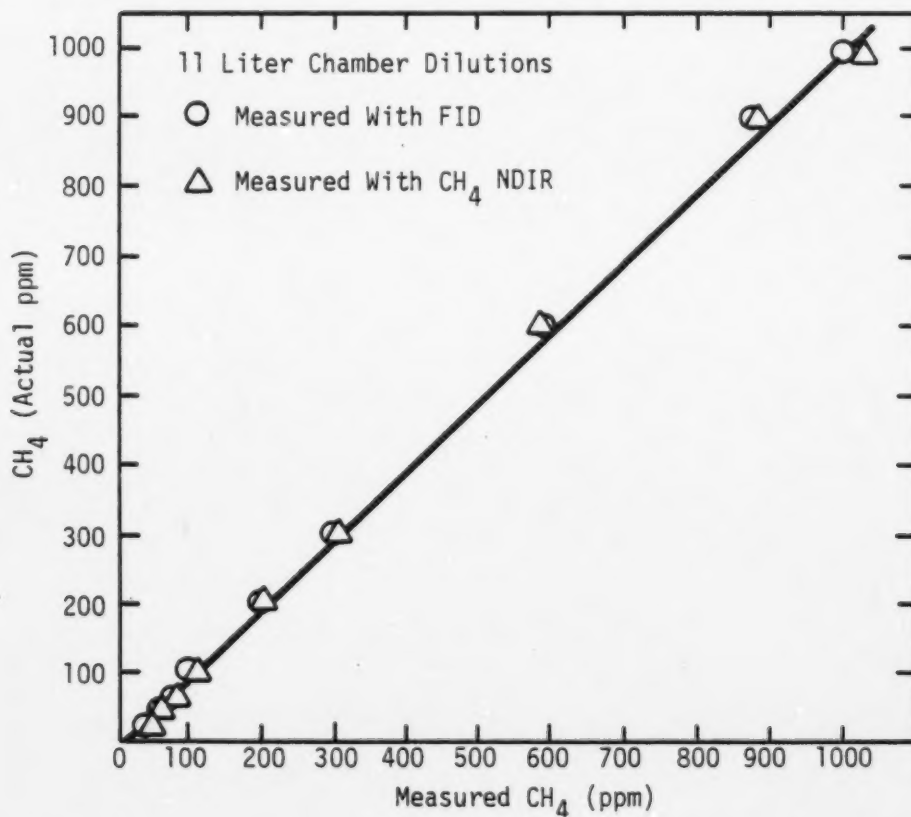
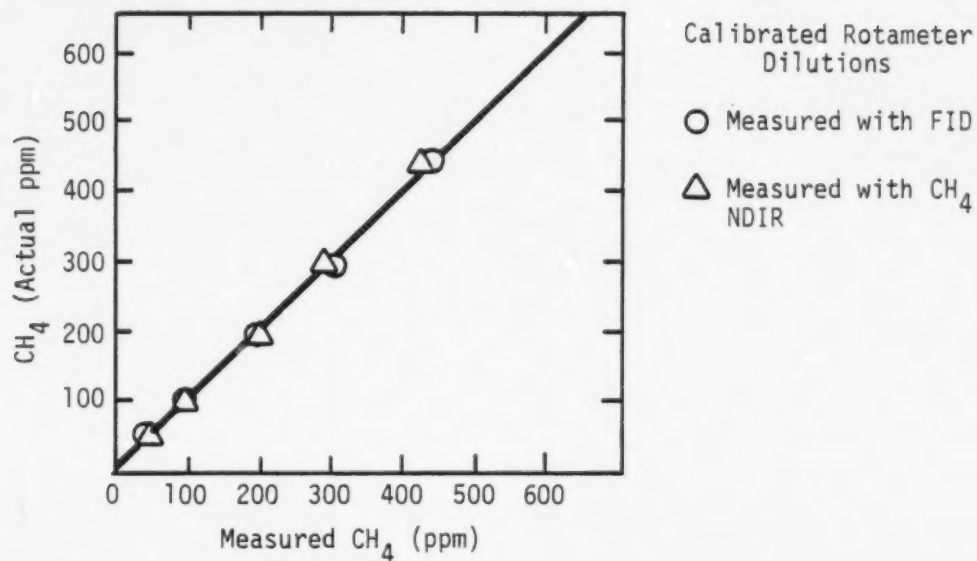


Figure 2-1. Linear responses verification for FID and CH<sub>4</sub> NDIR: dynamic flow calibration and static

A second series of tests was conducted to (1) establish the relative response of the FID to hydrocarbon type, and (2) determine the extent to which interfering gases bias the analyzer readings. To this end, a sampling/blending system was built whereby CO, CO<sub>2</sub>, CH<sub>4</sub>, C<sub>2</sub>H<sub>2</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>6</sub>, or C<sub>3</sub>H<sub>8</sub> could be blended with either N<sub>2</sub> or 995 ppm CH<sub>4</sub> in air and delivered through the sampling system to any one of all three of the analyzers to be evaluated. The gases of interest were introduced through calibrated rotameters or using a syringe drive.

The sampling/blending system was first used to determine the relative response of the FID to light hydrocarbons typical of those present in stack exhausts. The instrument was calibrated with a commercially prepared standard mixture of CH<sub>4</sub> (300 ppm  $\pm$  30 ppm) in air. Mixtures were prepared which consisted of either CH<sub>4</sub>, C<sub>2</sub>H<sub>2</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>6</sub>, or C<sub>3</sub>H<sub>8</sub> in N<sub>2</sub>. A sample of this mixture was analyzed by the instrument to determine the response factor curves shown in Figure 2-2.

As expected, the response of the FID was shown to be a function of carbon number and was linear with concentration over the range tested. The response was shown to be higher for the unsaturated hydrocarbon than for the corresponding saturated hydrocarbon. The instrument was then checked for response from mixtures of CO and CO<sub>2</sub> in N<sub>2</sub> to determine the extent of interference. The instrument did not respond to either CO or CO<sub>2</sub> up to levels of 500 ppm and 4 percent, respectively. The CH<sub>4</sub> NDIR analyzer was then subjected to the identical mixtures to evaluate interference from other species. The response of the analyzer (Figure 2-3) was found to be greatest for CH<sub>4</sub>, although the response to C<sub>2</sub>H<sub>6</sub> and C<sub>3</sub>H<sub>8</sub> was significant. No response was observed to C<sub>2</sub>H<sub>2</sub> (500 ppm max), CO (500 ppm max), or CO<sub>2</sub> (4 percent max).

Figure 2-4 shows the response of the CO analyzer to CO, CO<sub>2</sub>, and hydrocarbons. The instrument did not respond to hydrocarbons (500 ppm max). The instrument did, however, respond to levels of CO<sub>2</sub> typical of those present in stack exhaust. The CO yielded a reading of 10 ppm for 4 percent CO<sub>2</sub> and 30 ppm for 13 percent CO<sub>2</sub>. Thus, a baseline adjustment must be employed at low concentrations of CO.

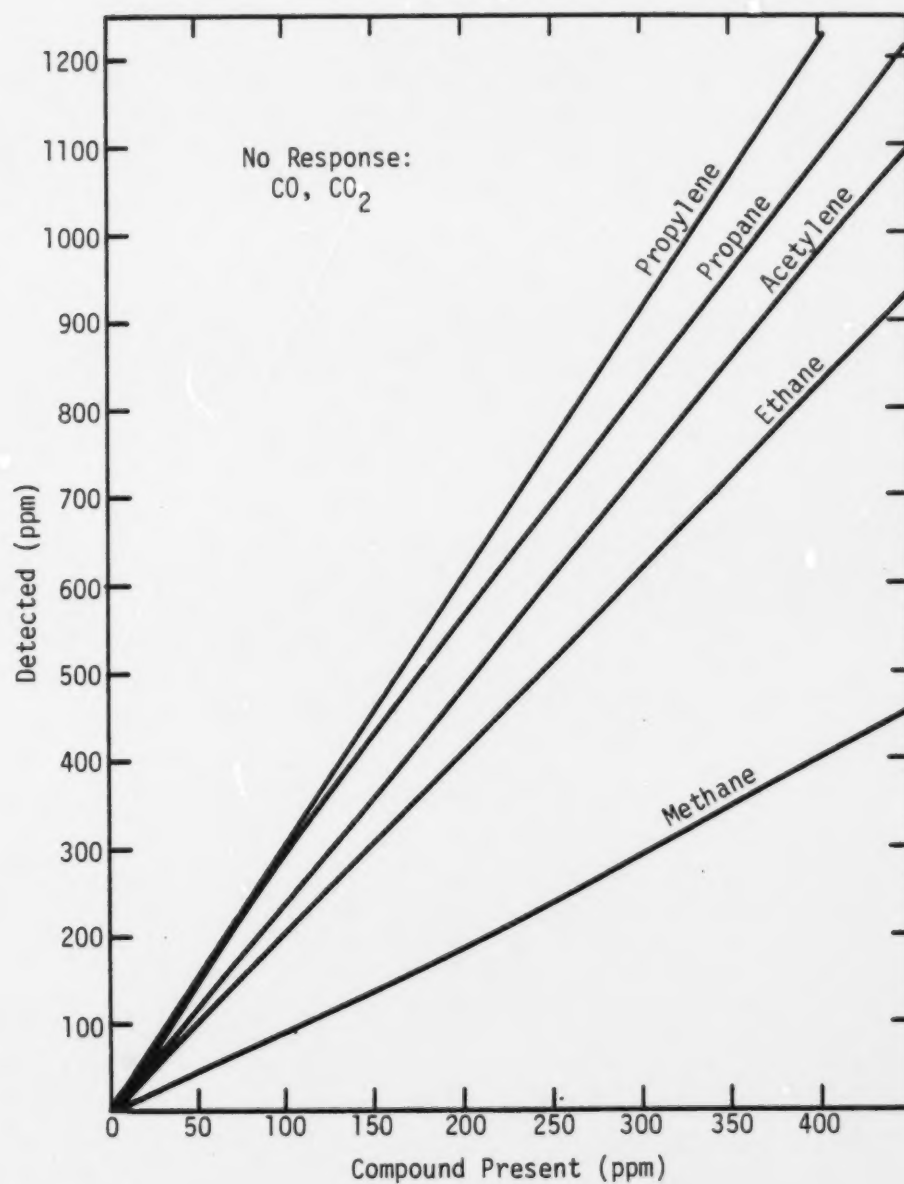


Figure 2-2. Relative response factors for FID.

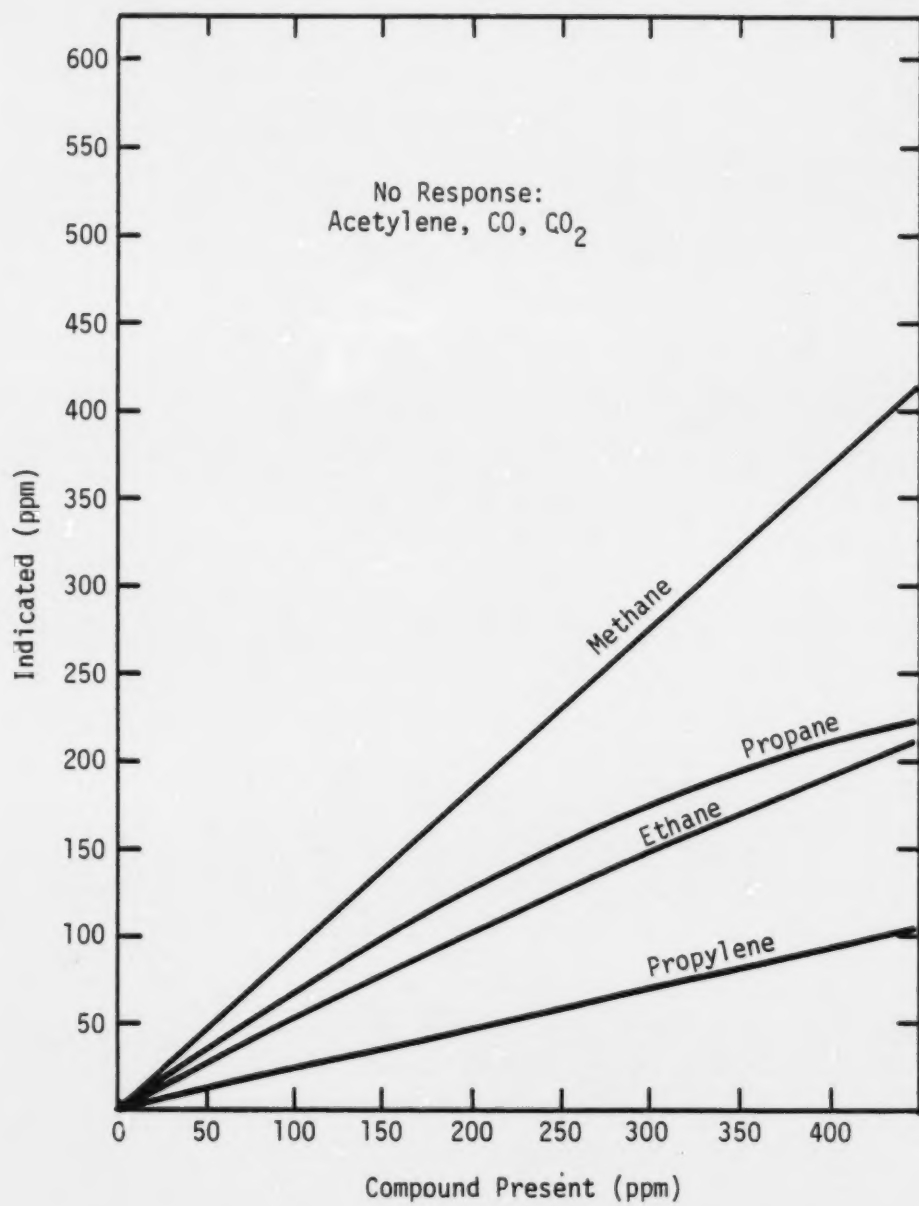


Figure 2-3. Relative response factors for CH<sub>4</sub> NDIR.

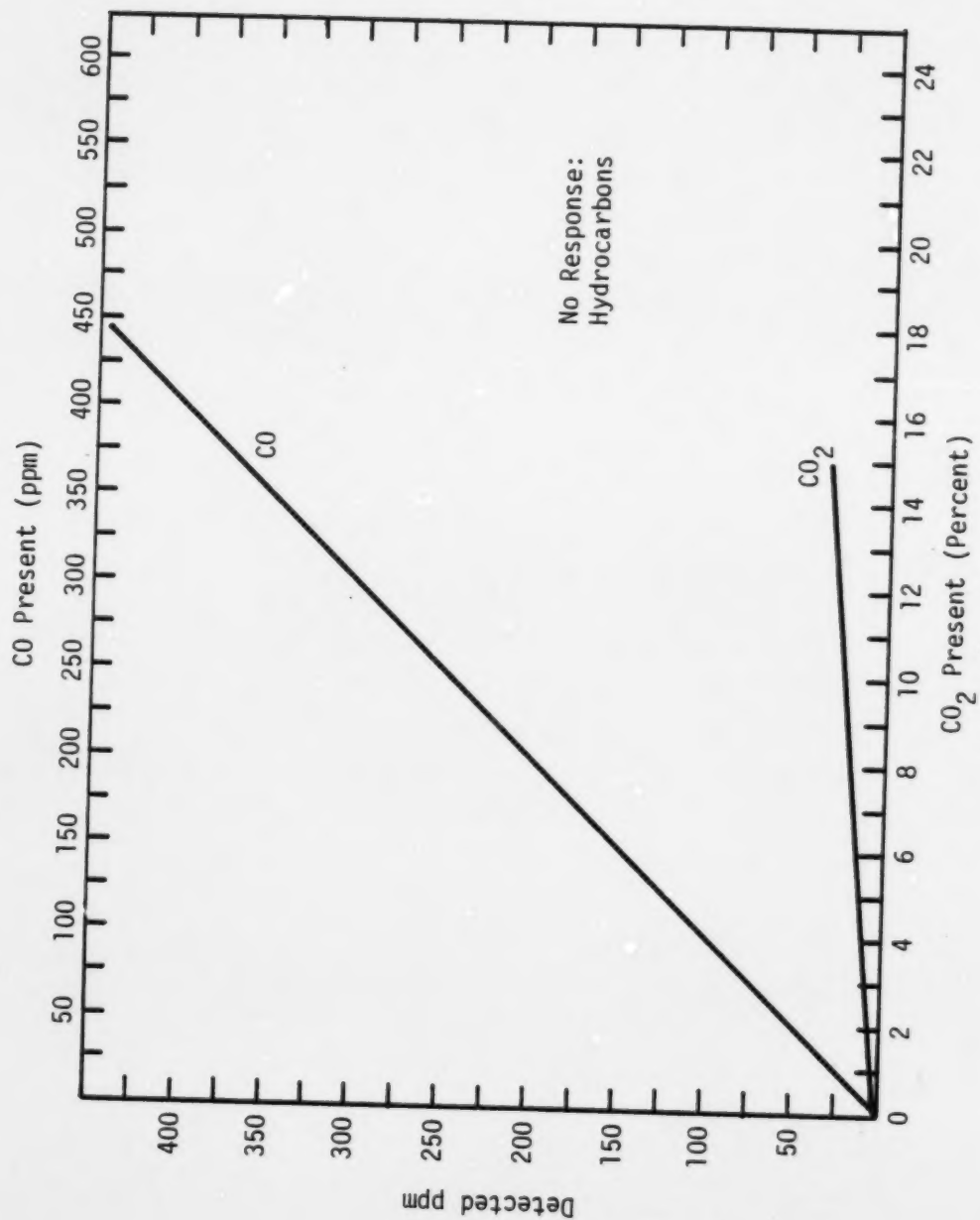


Figure 2-4. Response factors for the CO analyzer.

The next series of experiments involved measuring  $\text{CH}_4$  in the presence of other light hydrocarbons to determine if a measurement bias occurred as a result of a synergistic response. Figures 2-5 and 2-6 show the results of these tests. The response of each hydrocarbon noted was measured both with and without the addition of 100 ppm of  $\text{CH}_4$  to the sample stream. If no synergistic interference occurred, the response would be expected to increase by exactly 100 ppm when  $\text{CH}_4$  was added. This was the case.

The series of experiments just described examined potential interferences using mixtures of known composition. The final set of experiments examined response factors in an effort to locate unanticipated interferences from a stack effluent composition typical of practical devices. A laboratory combustor was used to produce a representative stack gas. The sampling/blending system was used to blend known amounts of hydrocarbons, CO, and  $\text{CO}_2$  with the stack gas. Measurements were then made in the same manner as the previous tests. Figure 2-7 shows that measurement of  $\text{CH}_4$  and hydrocarbons can be made with the FID and  $\text{CH}_4$  NDIR in a stack exhaust gas without interference from water and other constituents of an exhaust gas and is within reasonable error limits (accuracy better than  $\pm 5$  percent).

### 2.3 Turbulent Flame Reactor

The Turbulent Flame Reactor (TFR) was designed to provide a turbulent liquid spray flame which simulates the environment in hazardous waste liquid injection incinerators including swirl, recirculation, broad drop-size distribution, and high variation in droplet number density. It was particularly important that the reactor be capable of simulating the compound escape mechanisms that can occur for flame zones of liquid-injection incinerators. Very high heat removal rates were utilized to quench postflame reactions. Thus, destruction which occurred within the turbulent diffusion flame was emphasized over nonflame decomposition typical of that which can occur in the postflame region. The reactor design is based on a configuration for which aerodynamic field data are available (Baker et al., 1975).

The reactor consisted of a swirling air/liquid spray burner firing into a 30.5-cm-diameter by 91.5-cm-long water-cooled cylindrical enclosure shown in Figure 2-8. The water-cooled cylinder was made of 304 stainless steel

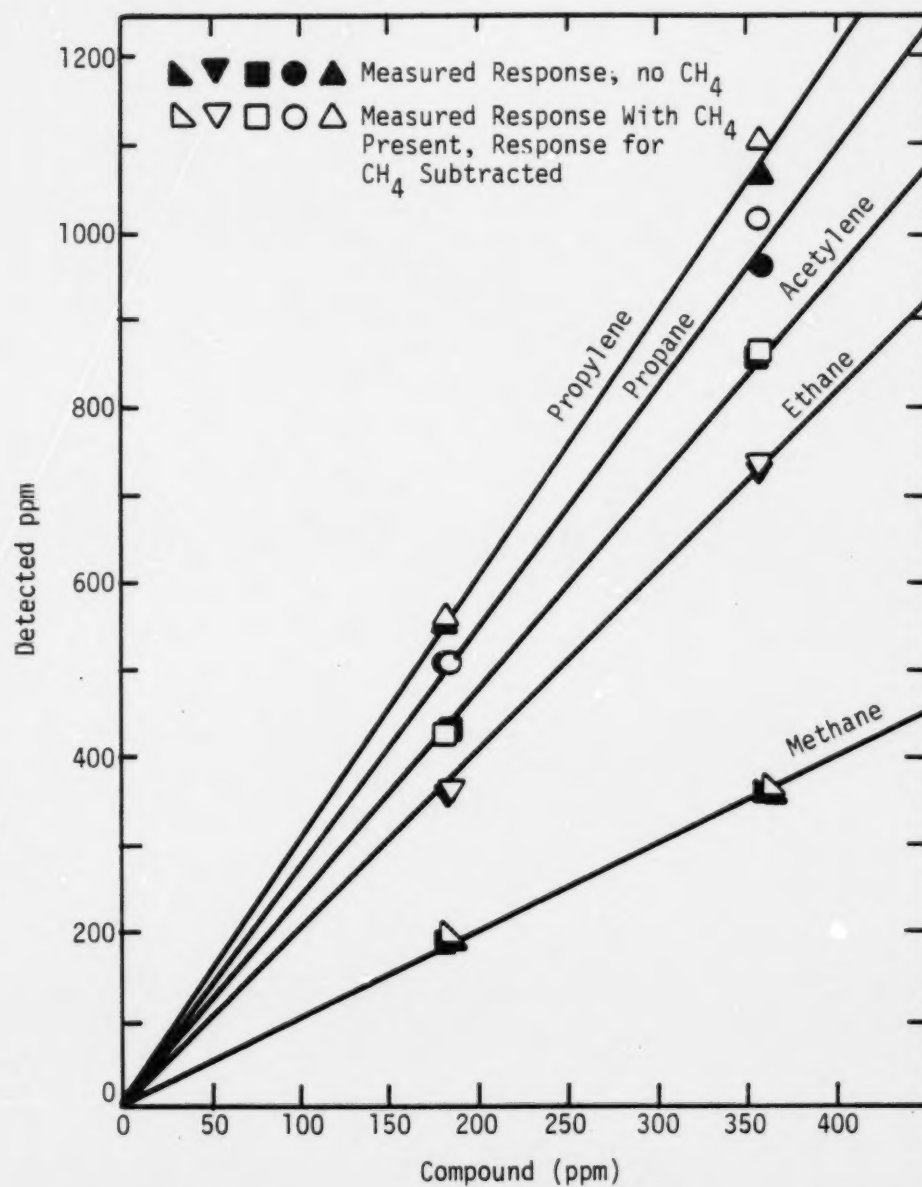


Figure 2-5. Hydrocarbon measurement in the presence of  $\text{CH}_4$  for the FID.

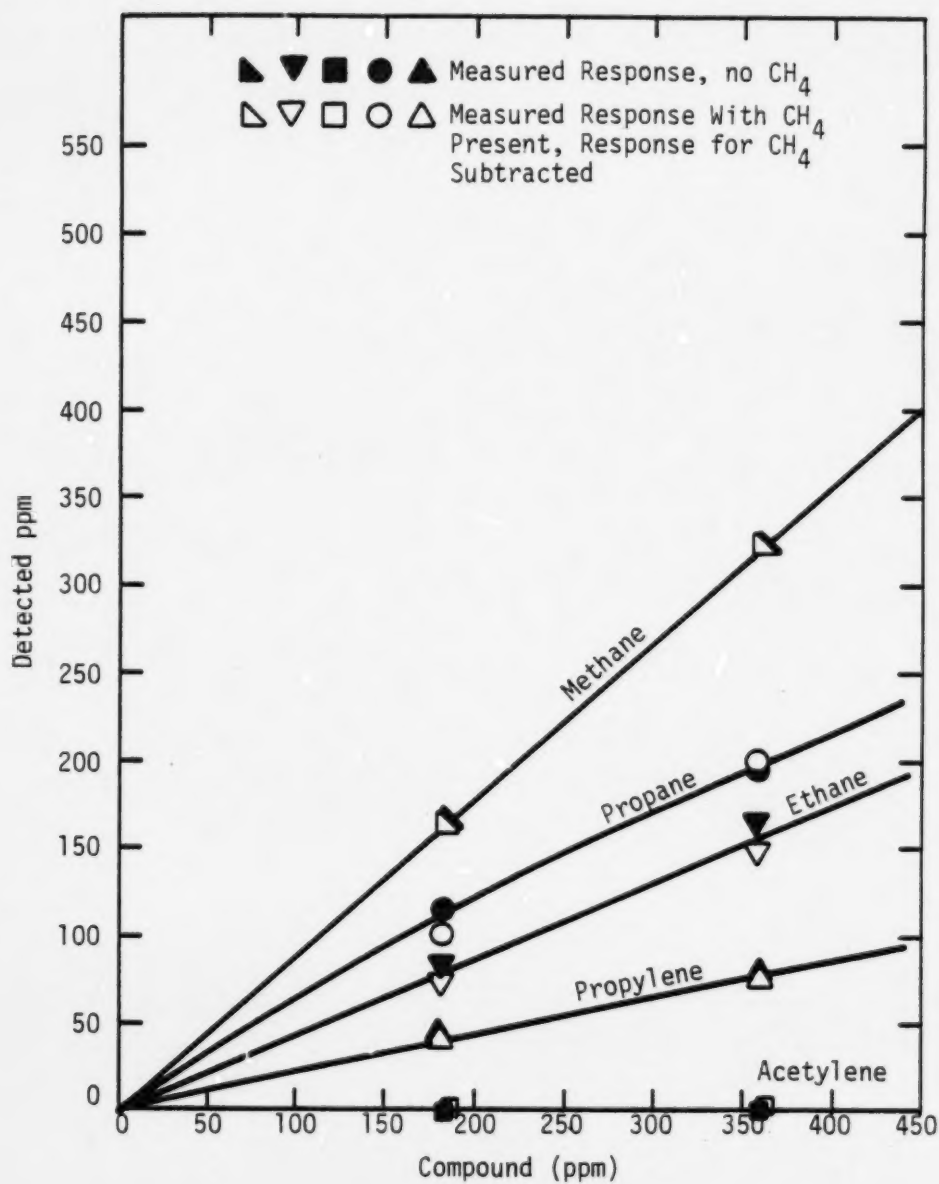


Figure 2-6. Hydrocarbon response in the presence of  $\text{CH}_4$  for the  $\text{CH}_4$  NDIR.

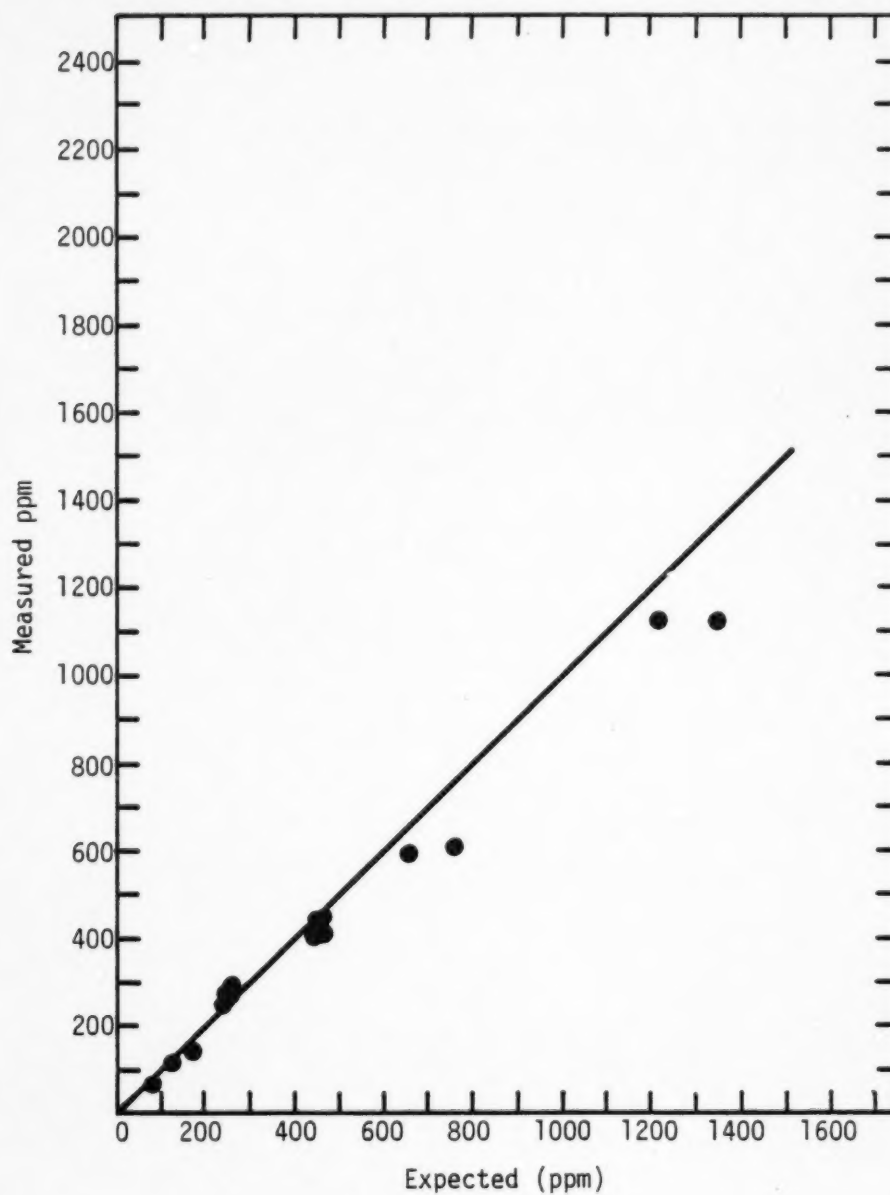


Figure 2-7. Microspray syringe addition of  $\text{CH}_4$  to actual exhaust wet sample gas, as measured with FID and  $\text{CH}_4$  NDIR.

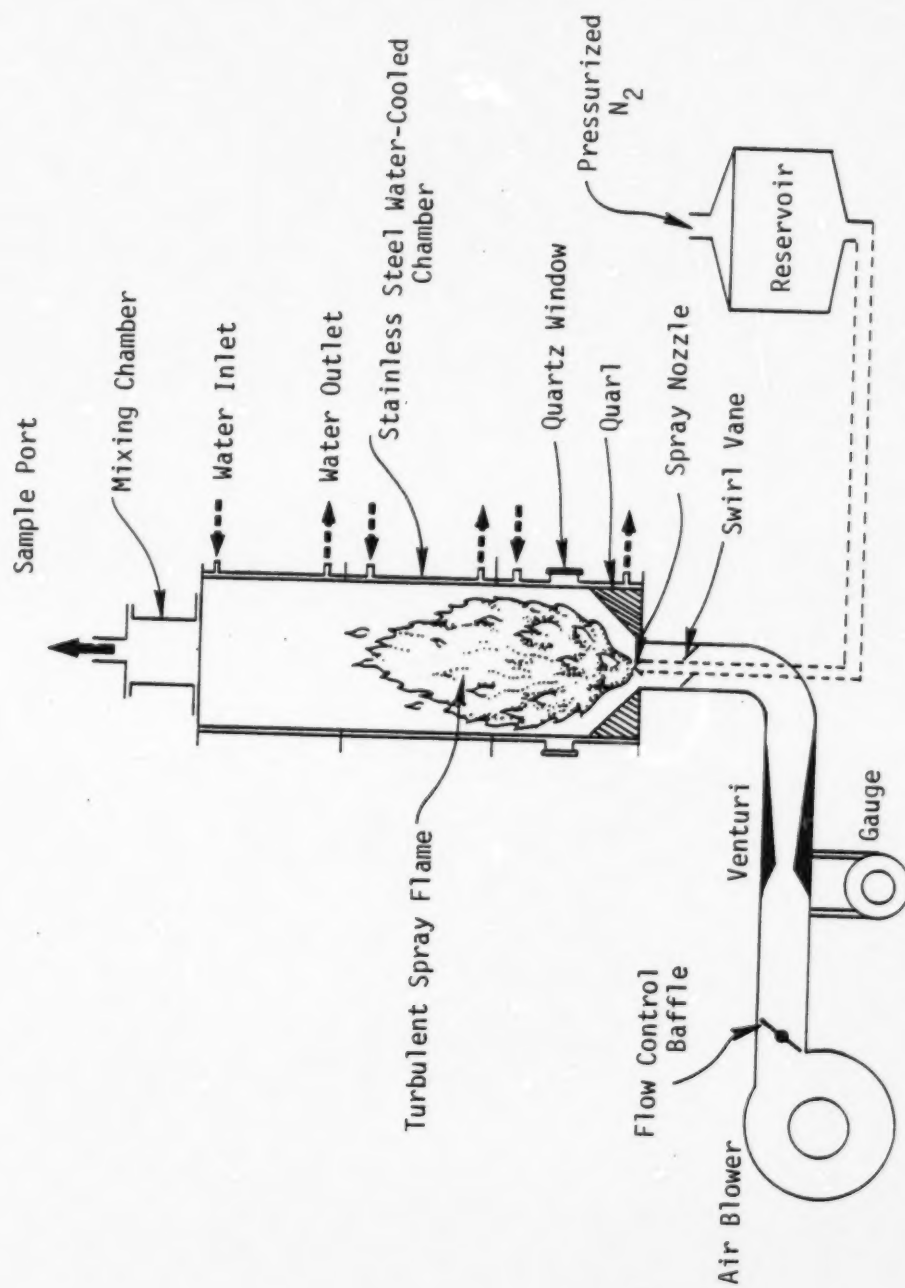


Figure 2-8. Turbulent flame reactor.

and formed into three interchangeable segments which were joined by flanges and gasketing. The lowest segment had four sight glass ports, one of which was used for flame ignition. The reactor top plate contained an exhaust fitting which included the sampling ports, and a Vycor window which provided an axial view of the flame.

The burner consisted of a pressure atomized nozzle (Delavan WDA series) located level with the bottom plate of the reactor as shown in Figure 2-9. The main burner air was introduced through the annular space around the nozzle. Variable area flow constrictors could be fixed into this space to vary burner air velocity independently of air flow rate. Interchangeable swirl vanes were placed into the gap between the constrictor and the nozzle shaft. The vane angle was set to provide a swirl number of unity for the present study. To provide a smooth entry of air into the burner and to prevent corner recirculation, a castable refractory quarl was placed in the lower water-cooled segment. As shown in the figure, this was in the form of a 45-degree cone.

The liquid fuel feed system consisted of a pressurized storage tank. The fuel-flow vs. tank-pressure calibration is discussed in Appendix A. The tank was pressurized with bottled nitrogen and the pressure was regulated with a two-stage bottle regulator. The burner air flow was supplied by a high-pressure-head rotary blower and was metered with a venturi flow meter. The calibration is discussed in Appendix A.

#### 2.4 Analytical Systems

The sampling system for the Turbulent Flame Reactor (TFR) was designed to measure (1) DE, (2) intermediate species ( $\text{CO}$ ,  $\text{CH}_2$ ,  $\text{THC}$ ), (3) major products of combustion (e.g.,  $\text{CO}_2$ ), and (4) excess oxygen ( $\text{O}_2$ ). A schematic of the system is presented in Figure 2-10.

The sampling system for continuous monitoring measurements consisted of 1/4" SS probe, a heated in-line filter, and a heated line with a tee. One line from the tee went first to a water-condenser, then to the  $\text{CH}_4$  analyzer,  $\text{CO}$  analyzer,  $\text{CO}_2$ , and  $\text{O}_2$  analyzers in series. The other line off of the tee, a heated line, was directed to the hydrocarbon analyzer.

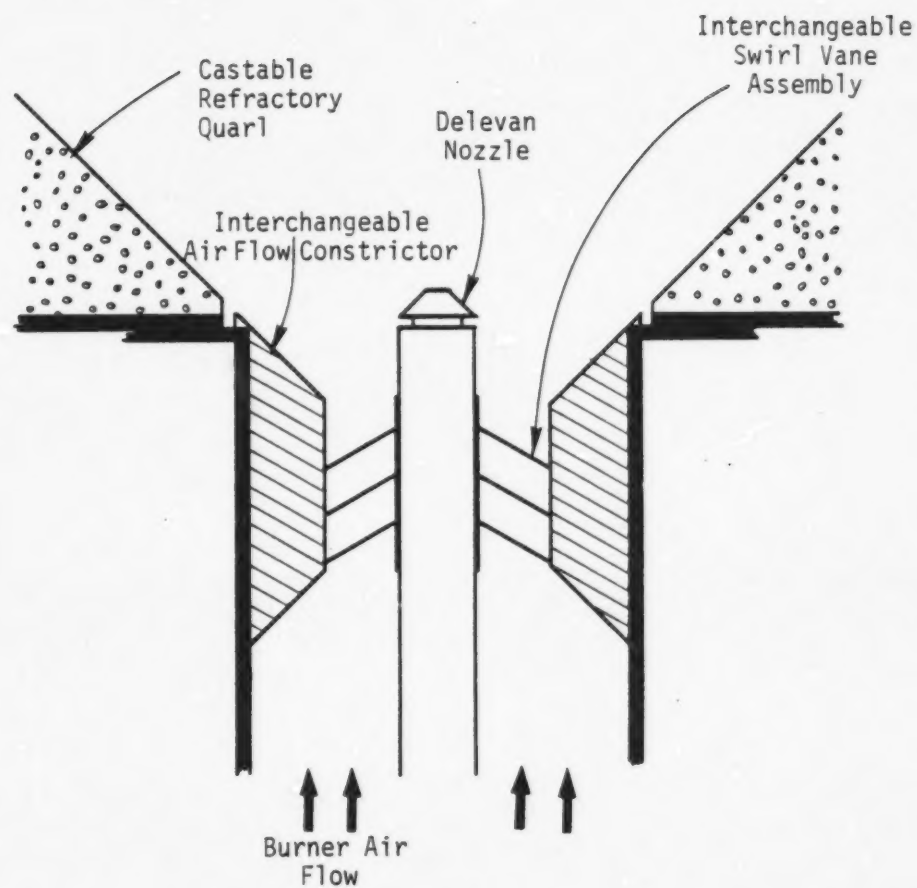


Figure 2-9. Turbulent flow reactor burner detail.

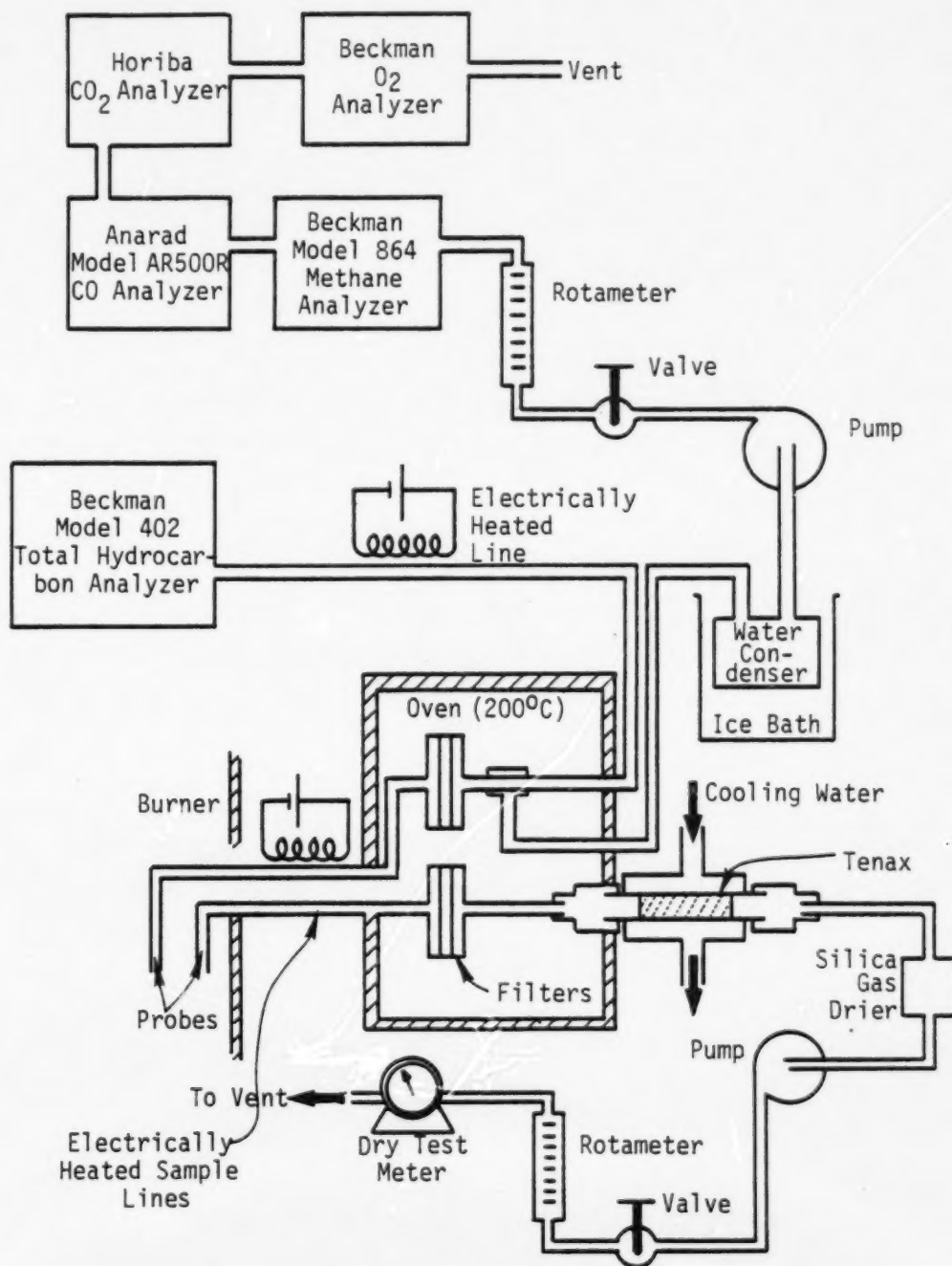


Figure 2-10. Sampling system for turbulent flame reactor.

The sampling system for the test compound destruction measurements also consisted of 1/4" SS probe and heated in-line filter. The details of the system design, calibration, determination of compound breakthrough volumes, and minimum sensitivity tests are discussed in Appendix B. The technique is generally based on the method of Parson and Metzner (1975) which consists of the adsorption of waste compound from a known quantity of sample of gas into Tenax-GC. This is accomplished by passing sample gas through an externally water-cooled Pyrex cartridge packed with Tenax. At the conclusion of sampling, the cartridge is thermally desorbed and the contents analyzed by Flame-Ionization Gas Chromatography (GC-FID). The procedure is to insert the cartridge into the helium carrier gas line so that the helium flows sequentially through the cartridge, the Porapak-Q column and the FID. The cartridge is placed within an aluminum block heater which heats the cartridge to 120°C for a sufficient time to desorb the test compounds and deposit them on the inlet of the room temperature GC-column. Following desorption, the column oven is temperature-programmed, the compounds swept by the carrier flow onto the column and separated, and the compound concentration measured.

The analytical technique is calibrated by sampling and analysis of known gas-phase concentrations of the test compounds. The sampling flow rate was optimized and the breakthrough volumes for each compound were determined to be greater than the sampling-volume volume; these tests are detailed in Appendix B.

The Tenax-GC technique was selected because of its high sensitivity (1.5 ppm or 99.995 percent DRE in the TFR) and the relatively rapid sample turnaround time (1.5 hr). The technique is compatible with the TFR in that test compounds, and products of incomplete combustion were adequately separated. Repetitive calibration tests have indicated an inherent experimental scatter that corresponds to  $\pm 5$  percent at the 90 percent confidence level.

### 3.0 RESULTS

In this section, results are presented for the incineration of representative waste compounds in the Turbulent Flow Reactor (TFR). In particular, the exhaust measurements of intermediate species and Destruction Efficiency (DE) of test compounds are presented for a range of operating conditions from high efficiency to low efficiency. (Note: Destruction and Removal Efficiency (DRE) cannot be used because in the present study there was no stack gas cleaning equipment before the measurement point.) The low destruction efficiency conditions were induced by operating the TFR at the following conditions typical of off-design performance:

- Fuel-rich operation
- Excessively fuel-lean operation
- Poor atomization quality
- Flame quench

#### 3.1 Influence of Stoichiometry

Fuel-rich and fuel-lean operation was accomplished by holding the load constant and varying the percent theoretical air. A constant fuel flow rate was set at the beginning of a test run and the burner air flow was varied to produce a range of theoretical air from approximately 60 percent to 400 percent. To assess the effect of load, this air flow variation was performed for three fuel flows: 3.8, 5.7, and 2.8 liters per hour. Each fuel flow was delivered with a nozzle designed for the specified flow rate so as to maintain atomization quality relatively constant.

The results for the 3.8 lph fuel flow rate are presented in Figure 3-1. Mole fractions of total hydrocarbons,  $\text{CH}_4$ , and CO are plotted on a log basis to maintain the data points within a reasonable scale. The concentration of total hydrocarbons (THC) is at minimum at 180 percent theoretical air (TA). At settings in excess of 260 percent TA (fuel lean) or below 85 percent TA (fuel rich), the concentration of total hydrocarbons rises sharply, reaching levels in excess of 1000 ppm. Methane concentration ( $\text{CH}_4$ ) follows the same general trend as THC. The CO measurement

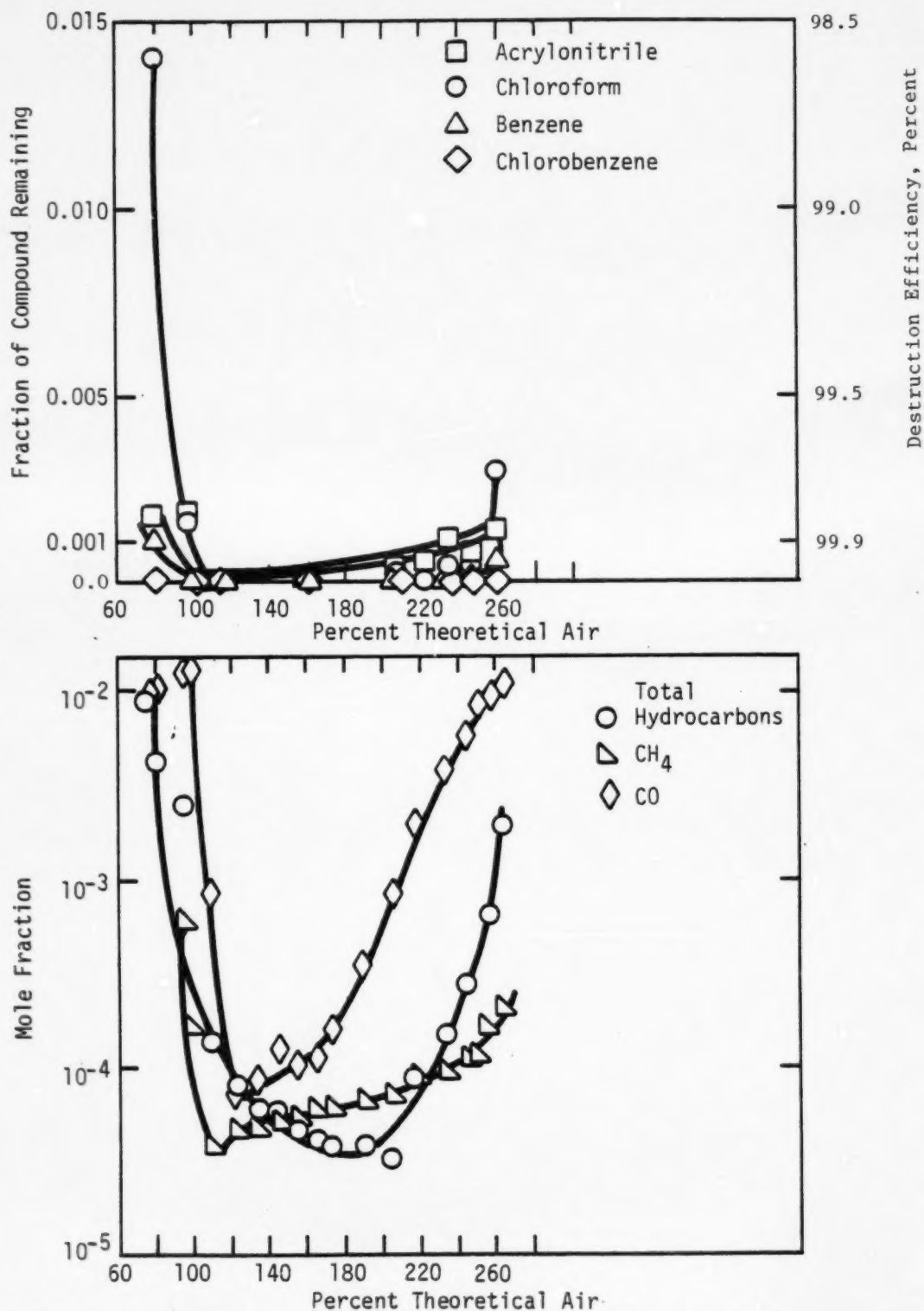


Figure 3-1. Continuous monitoring and DE data versus percent theoretical air for 3.8 lph fuel flow with a 3.8 lph nozzle.

provides the most sensitive response to mixture ratio, increasing sharply on either side of the minimum.

The corresponding DE data are plotted in Figure 3-1 in combination with the continuous monitoring data. Maximum DE (greater than 99.9 percent) occurs between 120 to 140 percent TA. Below 120 percent TA, chloroform exhibits the strongest tendency to persist. Above 150 percent TA, acrylonitrile is the first to indicate a decrease in DE. However, at about 260 percent TA, chloroform is again the most predominant concentration. Chlorobenzene indicates greater than 99.999 percent DE at all conditions. The same tests were conducted for fuel flow rates of 2.80 and 5.70 lph with similar results (Figures 3-2 and 3-3, respectively). Very lean conditions were obtainable for the 2.8 lph case due to the capabilities of the burner air delivery system. Mixture ratio affects the concentration of intermediate species in a similar manner as it affects the concentration of hazardous waste constituents in the exhaust. A range of optimum operation occurs, depending on the indicator used. Table 3-1 lists the ranges of optimum operation in terms of percent TA at the three different loads for each of the three performance indicators considered. Table 3-1 indicates that on the low excess air side of optimum operation CO emissions increase along with total hydrocarbons. However, for higher excess air operation the CO emissions increase before the total hydrocarbons, providing a more narrow range of optimum operating conditions. The DE data indicate that the CO and THC concentrations both increase well before low-efficiency conditions occur.

TABLE 3-1. RANGES OF OPTIMUM OPERATION FOR VARIOUS FUEL FLOW RATES  
BASED ON CONTINUOUS AND DE MEASUREMENTS

| Fuel Flow Rate (lph)            | 2.8                                       | 3.8     | 5.7     |
|---------------------------------|-------------------------------------------|---------|---------|
| Measurement                     | Range of Percent TA for Optimum Operation |         |         |
| CO Concentration                | 120-150                                   | 104-150 | 110-135 |
| Total Hydrocarbon Concentration | 120-210                                   | 100-200 | 110-140 |
| CH <sub>4</sub> Concentration   | 100-230                                   | 60-220  | 110-280 |
| Destruction Efficiency          | 104-200                                   | 66-220  | 110-230 |

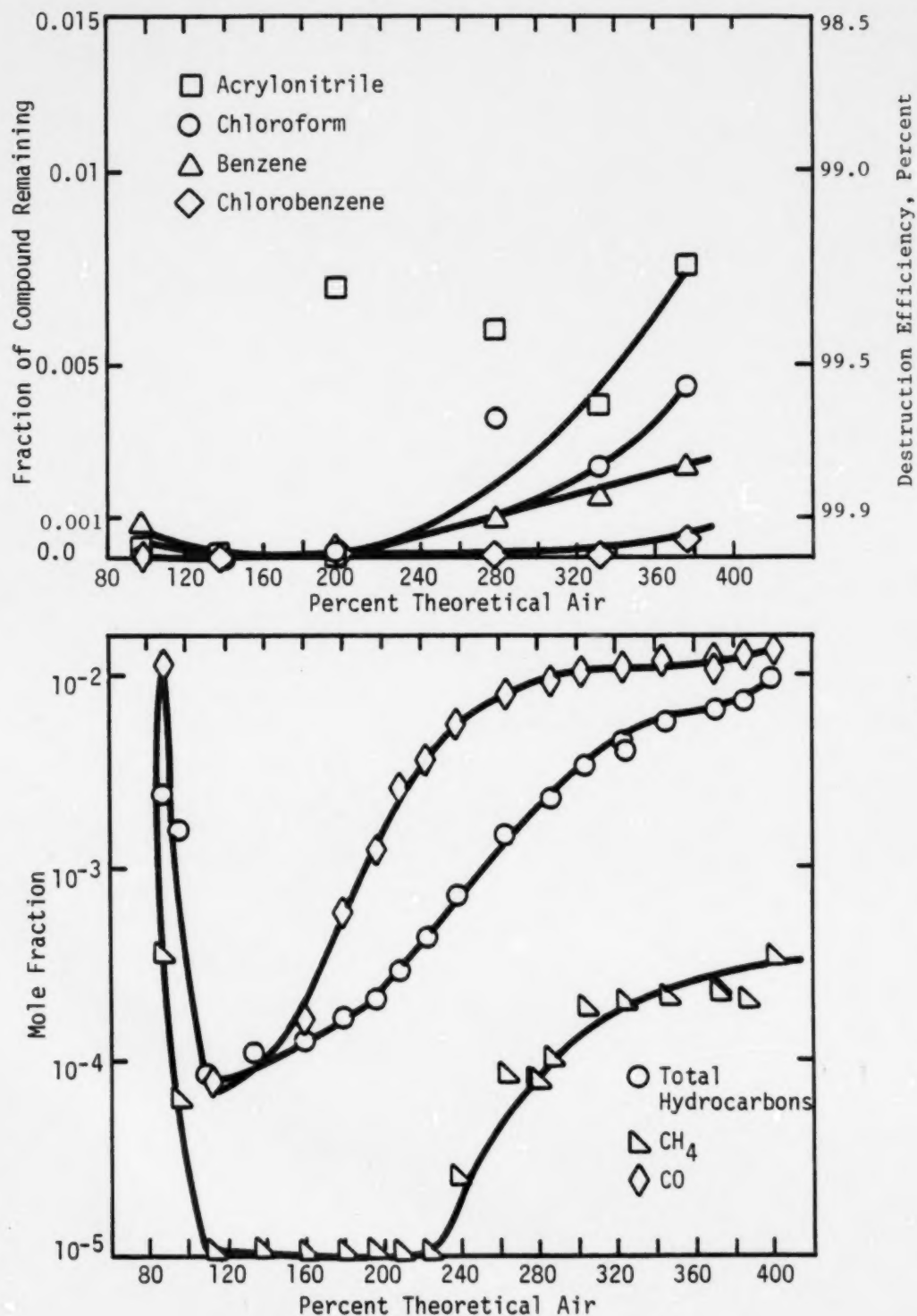


Figure 3-2. Continuous monitoring and DE data versus percent theoretical air for 2.8 lph fuel flow with 2.8 lph nozzle.

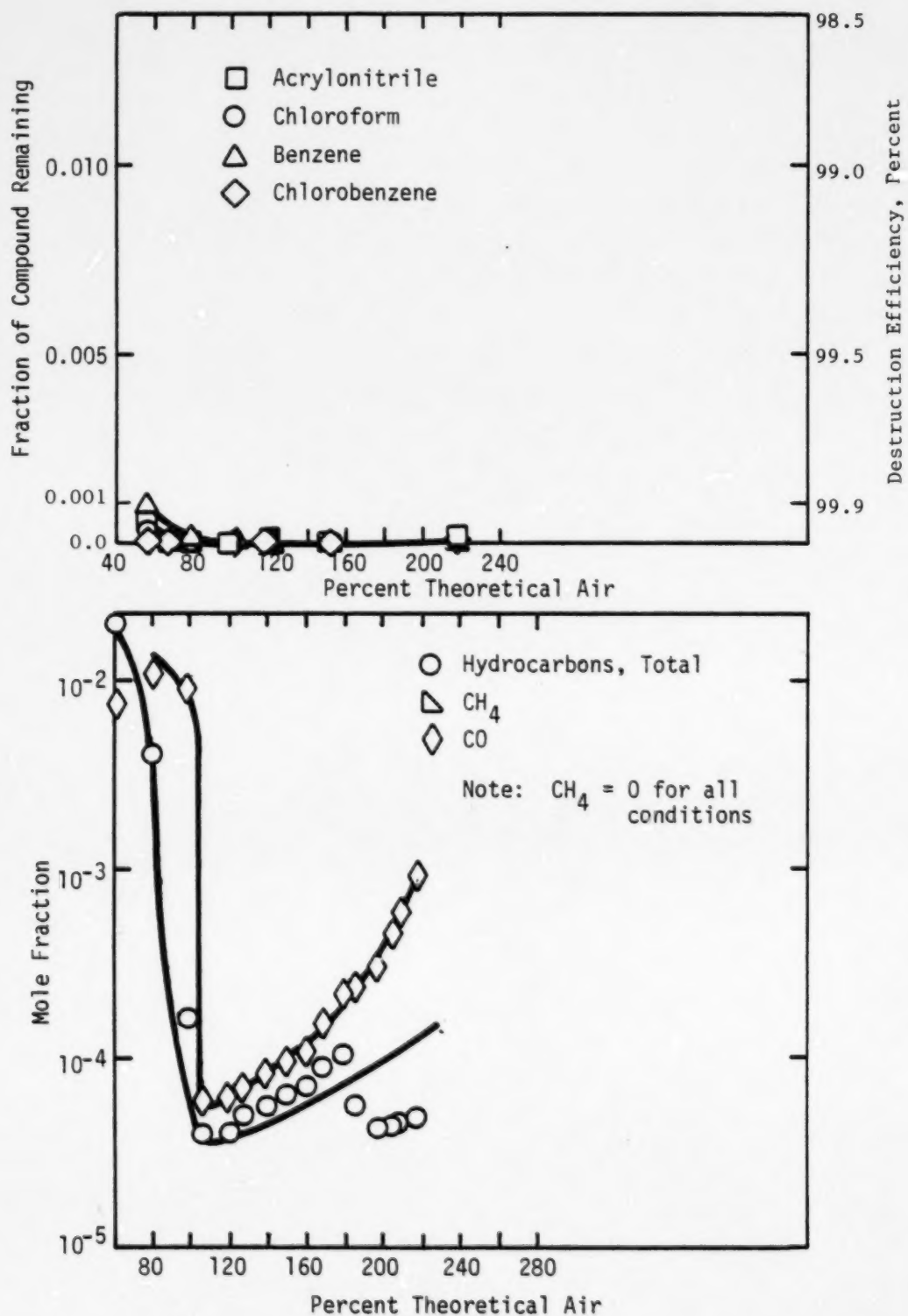


Figure 3-3. Continuous monitoring and DE data versus percent theoretical air for 5.7 lph fuel flow with 5.7 lph nozzle.

### 3.2 Impact of Atomization Quality

The second failure mode investigated was atomization quality. To generate poor atomization quality, the fuel nozzle employed was changed to a nozzle rated at a flow rate higher than the flow rate used. This resulted in a lower fuel pressure drop across the nozzle than design and hence the nozzle was operated at a poor condition. As before, the fuel flow rate was held constant and the burner air varied. The continuous monitoring results are plotted in Figure 3-4. The range of efficient operation as indicated by the CO concentration is more narrow than that observed for good atomization quality at the same fuel flow rate (Figure 3-1). Unlike [CO], the range of efficient operation as indicated by [THC] is not decreased by poor atomization. The methane concentration distribution actually widened.

The DE data indicate a degradation with poor atomization. The range of optimum performance as indicated by DE is smaller, and the minimum concentrations attained are generally higher. Again, both the [CO] and [THC] measurements provide sensitive indications of the onset of waste compound breakthrough for this failure mode. [CH<sub>4</sub>] did not prove nearly as sensitive in indicating poor efficiency for poor atomization.

### 3.3 Effect of Quench Coil

The final failure mode that was investigated is quenching by cold-surface impingement by placing a water-cooled coil directly into the flame. The fuel flow was again held constant at 3.8 lph and the burner air was varied. The results are presented in Figure 3-5. As with poor atomization, the optimum range indicated by [CO] and [THC] distribution narrows with the flame quench failure mode. In this case, the distribution for [CH<sub>4</sub>] narrows as well. The results for DE also indicate a more narrow range of efficient operation. Both [CO] and [THC] provide a sensitive indication of waste compound breakthrough for the flame quench failure mode. [CH<sub>4</sub>] is more sensitive for this failure mode than for poor atomization, but is not nearly as suitable an indicator of poor efficiency as are [CO] and [THC].

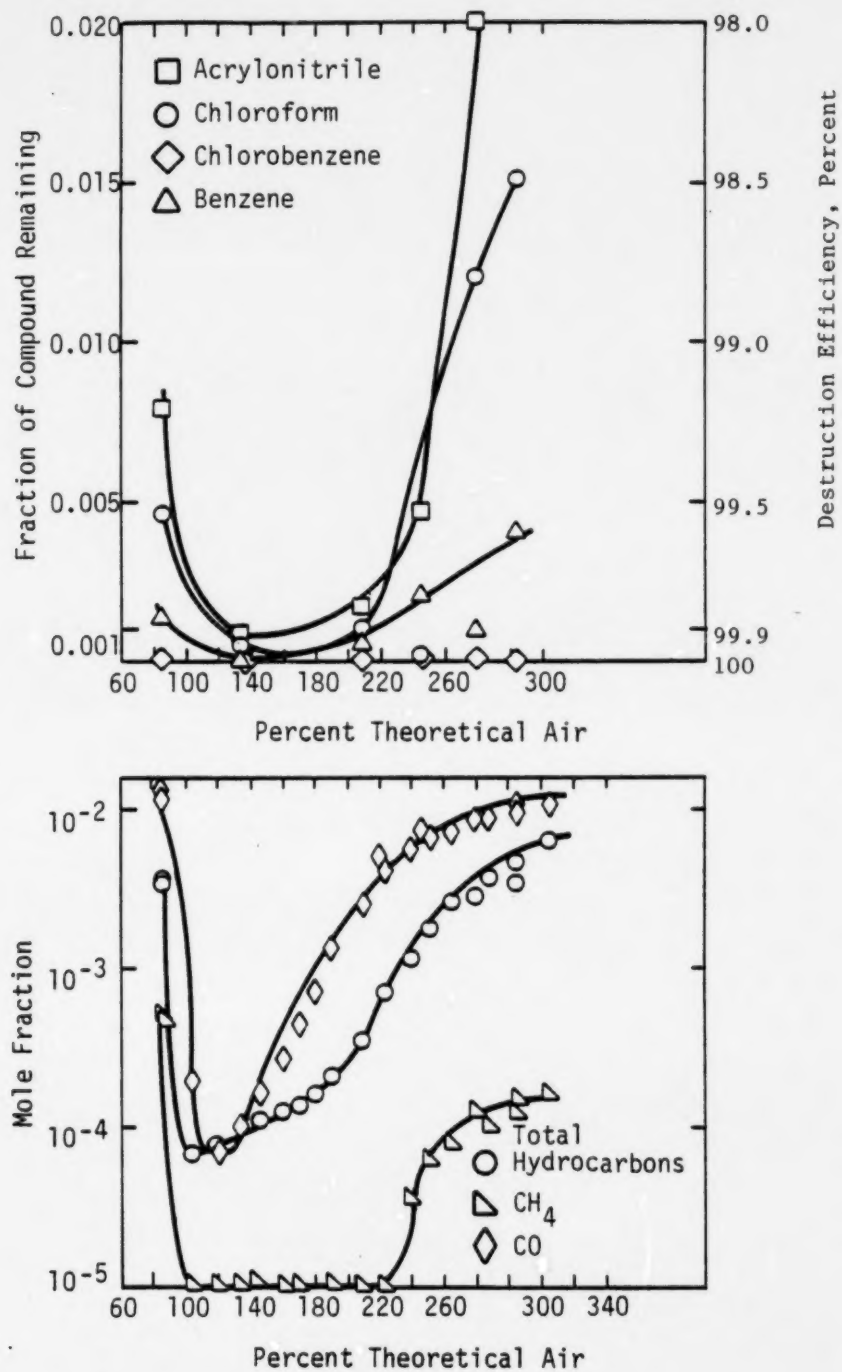


Figure 3-4. Continuous monitoring and DE data versus percent theoretical air for poor atomization.

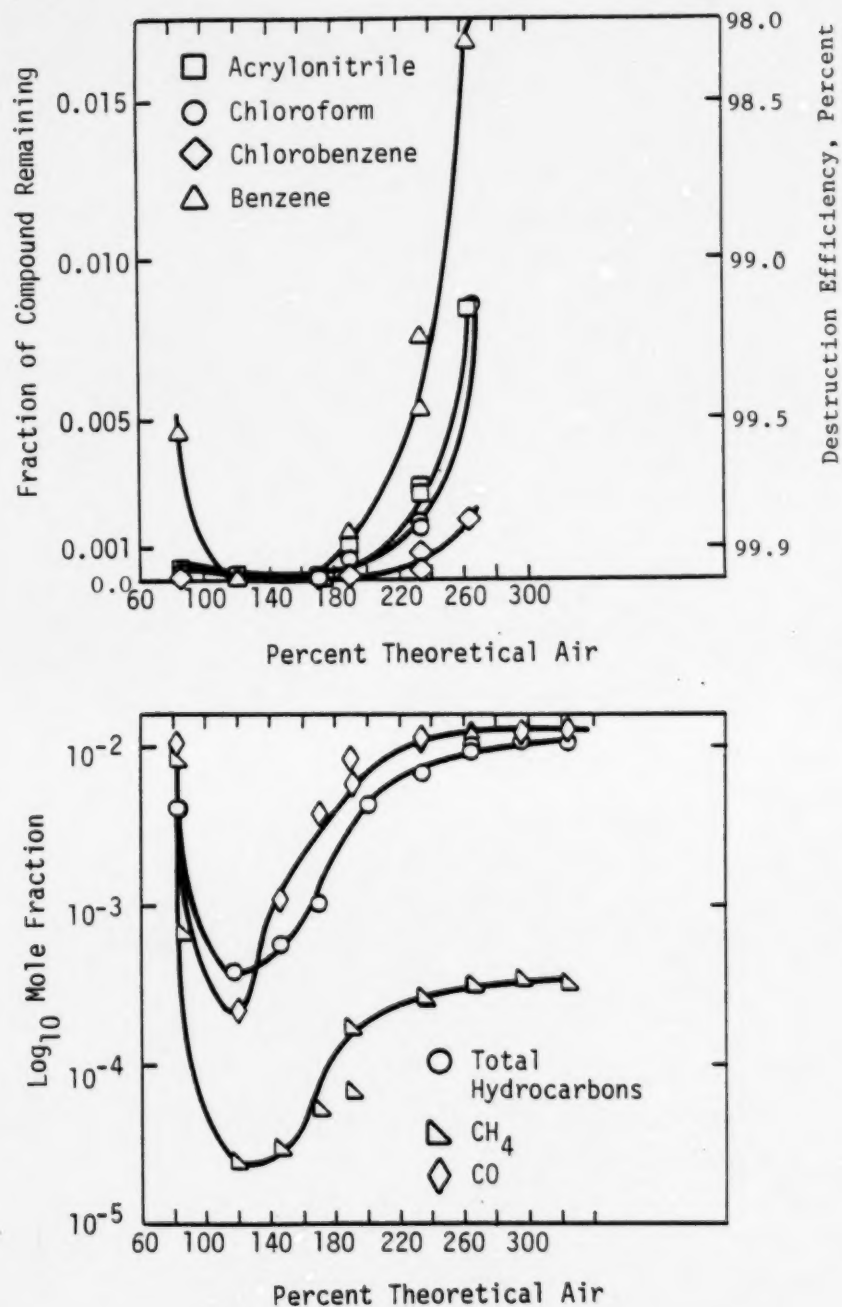


Figure 3-5. Continuous monitoring and DE data versus percent theoretical air for flame quenching.

#### 4.0 DISCUSSION, CONCLUSIONS, AND IMPLICATIONS

The purpose of this study was to determine the feasibility of utilizing real-time continuous exhaust measurements of combustion intermediates as a means of monitoring incinerator performance. The key issue was to determine if a direct correlation exists between DE and intermediate species concentration measurements. The intermediate species measurements were selected to be continuous and real-time. A comparison of the potential intermediate measurements with the availability of commercial instruments resulted in the selection of the Beckman 402 Total Hydrocarbon Analyzer (THC), the Beckman 864 NDIR methane analyzer, and an Anarad AR-500 NDIR CO analyzer. The response of each of these instruments was compared to DE measurements from a turbulent spray flame in order to experimentally determine if flame zone correlation exists.

The turbulent flame reactor (TFR) was designed such that the processes controlling DE in the flame, such as atomization quality, ballistic transport, turbulent mixing, flame quench, and flame-surface impingement, simulate those that control DE in the flame zone of a liquid injection incinerator. The cold walls of the TFR were designed to emphasize flame zone performance by quenching postflame reactions. As such, the TFR data do not directly address how postflame processes such as afterburners and gas cleaning equipment affect the flame-zone correlations.

The data presented in section 3 are cross-plotted to produce the DE-continuous monitoring correlations shown in Figure 4-1. These represent a broad range of operating conditions from high flame efficiency to low DE failure conditions. Two general types of correlations were observed between DE and the intermediate species measurements:

1. THC and CH<sub>4</sub>: The correlation between DE, THC, and CH<sub>4</sub> is nearly a proportional relationship; i.e., a linear increase in the intermediate concentration corresponds to a proportion increase in the hazardous component concentration.
2. CO: The CO correlation indicates that a significant increase in CO emissions is necessary before the exhaust concentration of waste compounds increases substantially.

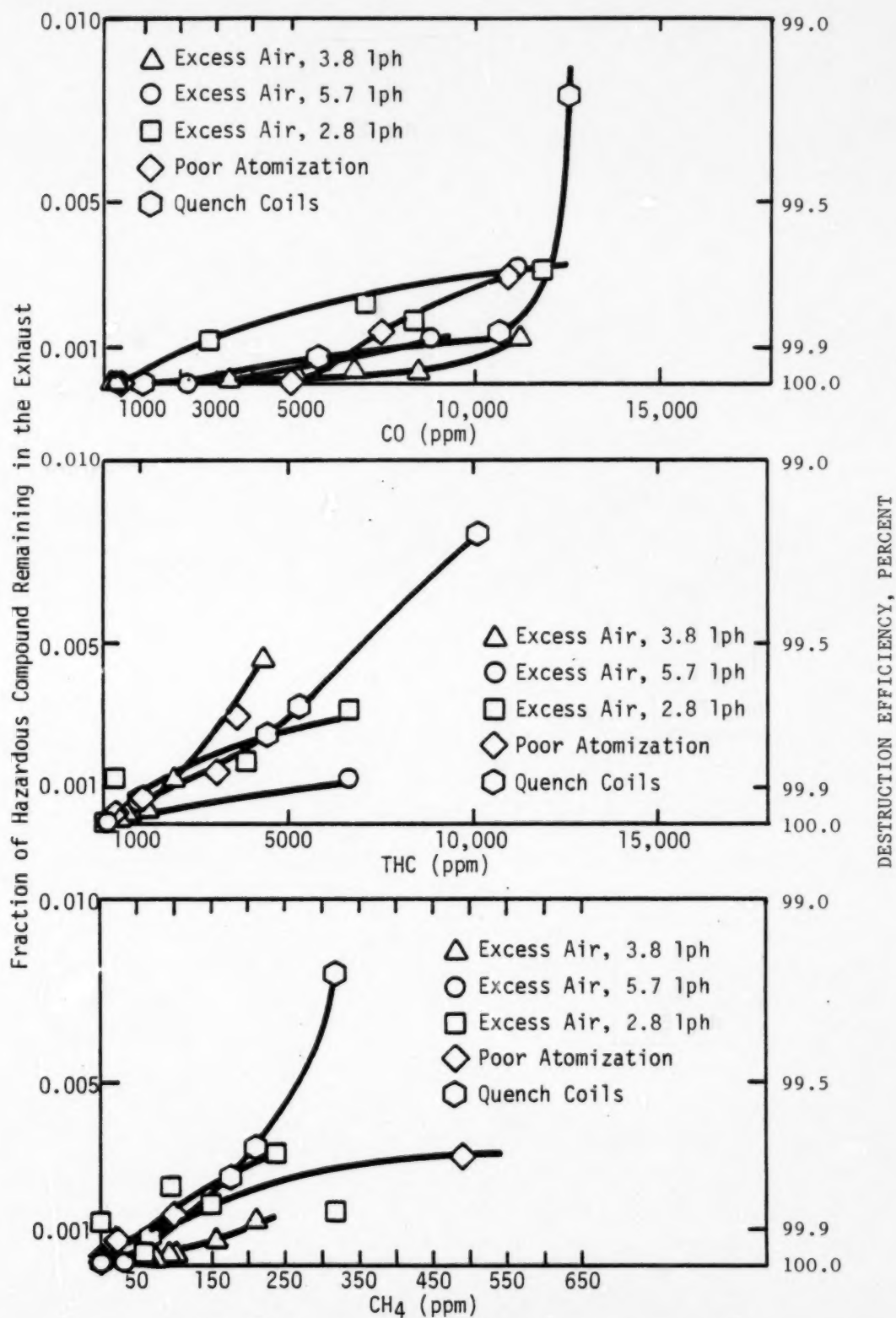


Figure 4-1. Fraction of hazardous compound remaining in the exhaust as a function of intermediate species concentrations.

Fundamental combustion kinetic studies (e.g., laminar flat-flames) indicate that hydrocarbon flames can be divided into two partially overlapping regions. In the first, hydrocarbon fuel is rapidly consumed by reaction with flame radicals (O, H, OH) to produce CO and water. In the second region, the CO is oxidized to CO<sub>2</sub> at a relatively slow rate. The flame can be made to operate inefficiently through, for example, a reduction in temperature or the addition of flame inhibiting compounds. The first manifestation of this inefficiency is release of CO because the hydrocarbon destruction reactions remain sufficiently fast to quantitatively remove organic molecules. It is only after the flame has become extremely inefficient that hydrocarbons are released, by which time the CO emissions are substantial.

Although a direct comparison between laminar flat-flame and turbulent flame results is difficult due to the fundamental difference between the processes, the reactions occurring in each are the same. These reactions are simply superimposed on different fluid dynamic backgrounds. Thus, a qualitative explanation for the flame zone correlations observed here would include:

- Since the hydrocarbon intermediates and the model waste compounds are made up of organic molecules, the flame destruction rate of each is similar, at least relative to the slower CO destruction rate.
- Decreased flame efficiency is evidenced by CO release while hydrocarbon intermediates and the waste compounds are still quantitatively destroyed.
- Further decreases in flame efficiency bring about a concurrent release of hydrocarbon intermediate and organic wastes due to the (relative to CO) similarity in their flame destruction rates.

These data support the following conclusions:

- A turbulent spray flame operating without afterburners or postflame gas cleaning is capable of achieving a DE of greater than 99.99 percent. This implies that careful design of efficient burners can cause the flame zone of an incinerator to perform most, if not all, of the legally required waste destruction.

- The data indicate that flame conditions which minimize CO, THC, and CH<sub>4</sub> emissions result in optimum waste DE. This indicates that maximum flame efficiency, as defined by the release of fuel and fuel fragments, also results in maximum waste destruction.
- Less than optimum DE performance was accompanied by increased release of intermediate species. This means that for all conditions examined in this study, a change in DE toward lower efficiency was always accompanied by an increase in CO, THC, and CH<sub>4</sub>.
- The range of conditions for optimum flame performance, as defined by CO, THC, and CH<sub>4</sub>, was found to be less than or equal to the range for high DE. This means that under some conditions, the flame performance could decrease without a significant decrease in DE. Even though the DE remains high, these conditions are clearly consistent with presence of other products of incomplete combustion (PIC) in the incinerator exhaust. There is also a potential that the PICs could be hazardous compounds and that these conditions would not represent environmentally acceptable operation.
- CO was found to increase significantly under some conditions in which the DE remained high.

Application of these results to the continuous monitoring behavior of a full-scale incinerator requires some assessment of how the postflame zone process, such as afterburners or scrubbers, affects the flame zone correlations. Due to the very low solubility of hydrocarbons and CO in aqueous solutions, incinerator scrubbing systems would not be expected to alter the continuous monitoring correlations for organic wastes. However, the afterburner may be expected to impact the postflame zone correlations. The aliphatic hydrocarbons that make up the bulk of THC, and in particular methane, are generally equally or more resistant to nonflame thermal destruction than the waste compounds upon which thermal testing has been performed. This indicates that monitoring THC and methane approach is potentially more conservative than indicated by the flame measurements. Thermal testing has not been performed on CO. However, detailed chemical kinetic predictions indicate that the nonflame thermal destruction rate of CO

is approximately the same as that for hydrocarbons (as opposed to the flame destruction rates in which the hydrocarbons predominate). Thus, no large alteration of the flame zone correlation would be expected.

The correlations shown in Figure 4-1 suggest that CO is possibly an overly conservative indicator of flame performance. That is, an incinerator shutdown procedure based on the response of a CO monitor may be environmentally safe but economically impractical. The results of this study suggest the following approach to incinerator monitoring and control:

- Use CO as an indicator of flame performance, but not as an incinerator shutdown criterion. This should provide a means of tuning the flame operating parameters.
- Use THC as a shutdown alarm to indicate potential waste compound release.

Use of these two instruments in tandem provides, through CO, a means of tuning for flame efficiency and, through THC, a means of indicating incipient waste emission and directing shutdown.

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APPENDIX A  
EXPERIMENTAL FLOW CALIBRATIONS

In this Appendix the techniques used to monitor the reactant flows to the turbulent flow experiments are discussed. In addition, the flow calibration procedures are described.

Burner air flow was measured by a Barco 3-in. ID venturi. A magnahelic gauge was used to indicate the pressure drop between the venturi taps. The calibration constant was obtained from the basic flow equations and was found to compare exactly with the manufacturers calibration curve. The calibration was:

$$Q_{\text{air}} = 44 \sqrt{\Delta P} \quad (\text{A-1})$$

where  $Q_{\text{air}}$  = flow rate of burner air (standard cubic feet per minute).

$\Delta P$  = magnahelic reading (inches water ).

A direct calibration check was not possible because of the high air flows. However, an indirect check was performed through burner stoichiometry measurements.

Burner fuel flow was set by the pressure on the fuel delivered to the nozzle. This pressure forced liquid through the nozzle orifice. Thus, the pressure-flow relation can be expected to be governed by Bernoulli's equation:

$$\Delta P \rho = V^2 / 2 \quad (\text{A-2})$$

where  $\Delta$  = fluid gauge pressure

$\rho$  = fluid density

$V$  = fluid velocity at orifice

This can be arranged to yield

$$\dot{m}_L = C D^2 \sqrt{\rho \Delta P} \quad (\text{A-3})$$

where  $\dot{m}_L$  = liquid flow

$C$  = system constant

Because of manufacturing variations, each nozzle was calibrated at several pressures. The results were well described by Equation A-3, which was subsequently used to interpolate between calibrated points.

## APPENDIX B

### ANALYTICAL TECHNIQUE FOR TEST COMPOUNDS

#### B.1 Introduction

The Tenax-GC sampling/analysis technique was selected for the measurement of the test compound destruction efficiencies for the following reasons:

1. High Sensitivity: The minimum sensitivity of the technique has been experimentally determined to be about 1.5 ppb, which corresponds to ~99.995% DE for the turbulent flow reactor at nominal operating conditions. Direct grab sample/GC injection techniques are simpler and are more rapidly performed but cannot measure to 99.99 percent DE.
2. Simple Operation/Rapid Turnaround: The principal competing technique, XAD-2, requires chemical extraction of the sample, a concentration step for low concentration samples, and GC analysis. With the Tenax-GC technique the sample cartridge is placed directly in the GC, desorbed and analyzed in a single operation. Thus, sample turnaround can be as low as one hour.

There are two principal limitations on the technique as it is presently employed. First, the compounds can pass through the Tenax with only partial adsorption (volumetric breakthrough). This is a particular problem for compounds with molecular weights below 150. Since all the test compounds fall below this molecular weight limit, breakthrough volumes were carefully checked for each. In general, XAD-2 avoids this problem because of higher compound specific breakthrough volumes. Second, the use of packed columns for separation of test compounds on the GC reduces the resolution of separation. The typical peak width is such that the successful separation of more than five compounds can be difficult due to peak interferences.

The technique, in summary, consists of the adsorption of test compound from a known volume of sample gas onto cooled Tenax. At the conclusion of sampling the Tenax cartridge is placed in the carrier gas line upstream of a packed column. The cartridge is electrically heated and the trapped compounds

are desorbed into the carrier gas. The compounds are trapped at the upstream end of the room temperature packed column. After desorption is complete the column is temperature programmed, and the compounds are separated and analyzed by a flame ionization detector (FID). The system is calibrated in two ways. First, dilute concentrations of test compounds in air are prepared in an 11-liter dilution tank. This gas is sampled and analyzed by the Tenax technique as if it were a normal sample. Second, direct liquid injections of test compounds onto the GC column were performed with a microliter syringe; this bypassed the Tenax. Comparison of the results of the two techniques indicates the presence or absence of systematic calibration errors and indicates if volumetric breakthrough has occurred. The occurrence of volumetric breakthrough was further tested by placing two cartridges in series and determining if any compound appeared on the second cartridge during adsorption.

The following section describes the analytical equipment, the calibration tests, the operating procedures, and miscellaneous verification work.

## B.2 Analytical Equipment

Sampling and Adsorption: The equipment is illustrated in Figure B-1. Exhaust gas samples were collected from the stack by an uncooled 6.35 mm OD (0.25-in.) stainless steel probe. After leaving the stack the probe was heat-taped and insulated to maintain a 200°C temperature. The sample passed through a filter (47 mm Gelman) in a 200°C oven. The hot sample stream passed through an externally water-cooled Tenax cartridge. The cartridge consists of a 120 mm long by 10 mm ID Pyrex tube packed with  $0.65 \pm 0.02$  grams of Tenax-GC (40-80 mesh). The adsorbent was held in place with small plugs of silianized glass wool. The sample line was connected to the cartridge by Ultra-Torr fittings. The entire cartridge was placed within a heat exchanger that flowed cooling water around the cartridge. The sample subsequently passed through a gas dryer, a rotameter, and a dry test meter. All connections upstream of the cartridge were either 316 stainless steel or 6.35 mm OD (0.25-in.) Teflon.

Desorption and Analysis: This system is based on a Perkin-Elmer Sigma 2 gas chromatograph with a Sigma-10 integrator/data station. The column is a 0.5-long, 3.18-mm OD (1/8-in.) Teflon tube packed with Porapak-Q. The 30 cc/min. carrier gas flow is maintained through the Tenax cartridge, the column,

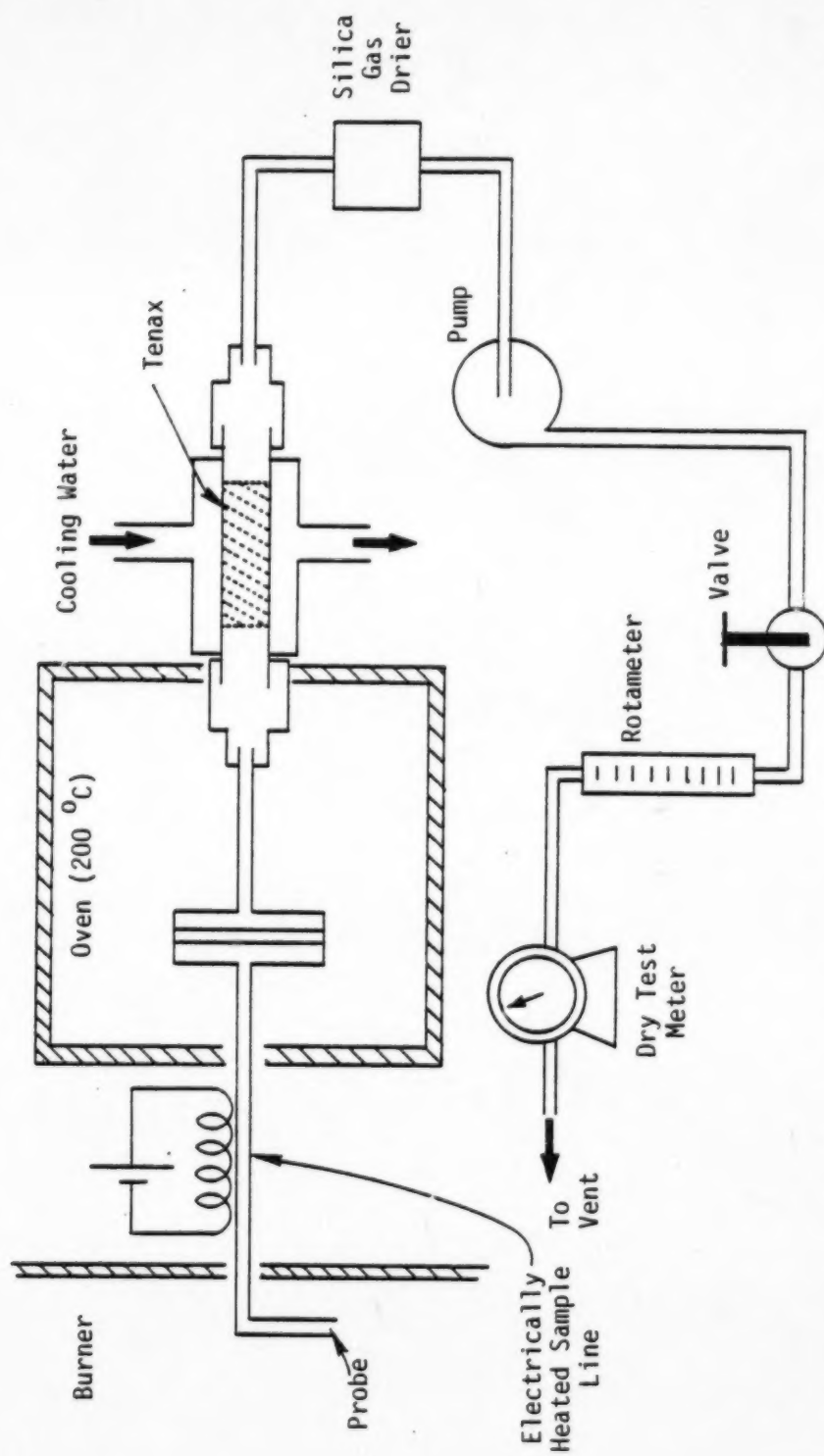


Figure B-1. Sampling and adsorption system.

and the FID, as shown in Figure B-2. The desorber is made from a 58-mm square aluminum block. The dimensions are detailed in Figure B-3. Eight 500-watt electrical cartridge heaters are imbedded in the block. The voltage to these is controlled by a variable transformer.

### B.3 Operating Procedures

Prior to use the Tenax cartridges are conditioned under a 20 cc/min. helium flow at 200°C for 45-min. Both before and after sampling the tube ends are covered with cellophane and refrigerated.

After the reactor condition has been set the cartridge is placed in the adsorption train, the cooling water started, and the sample flow opened. A sample flow rate of 0.23 liters/min. has been found satisfactory as discussed below. At the conclusion of sampling (2.3-liters or 10-min.) the cartridge is removed and refrigerated.

For analysis, the cartridge is connected into the GC carrier gas line and placed in the desorption block. The block is raised to 120°C and held at this temperature for 5-min. This time and temperature have been found sufficient to quantitatively desorb all of the test compounds. During desorption the GC oven is maintained at room temperature. As the compounds desorb, they are collected at the inlet of the GC column. The compounds do not start to separate at room temperature. If this was not the case, peaks would be broadened by the deposition of newly desorbed compound at the column inlet after separation had started. At the conclusion of the 5-min. desorption time the column was heated to 120°C, held at this temperature for 25 min., and programmed at 5°C/min. to 150°C. The FID gas flows were 71 cc/min. hydrogen and 442 cc/min. air.

The integrator output record consists of a chromatogram detector signal trace and a table of integrated peak areas. The trace is compared with the tabulated output to insure that the compound peaks are free of interferences, that the baseline boundary conditions were correctly constructed by the integrator, and that the presence of unanticipated peaks could be noted. Integrated peak area values were converted into ppm by use of the calibration curves and destruction efficiencies were calculated using the ppm anticipated from zero destruction operation.

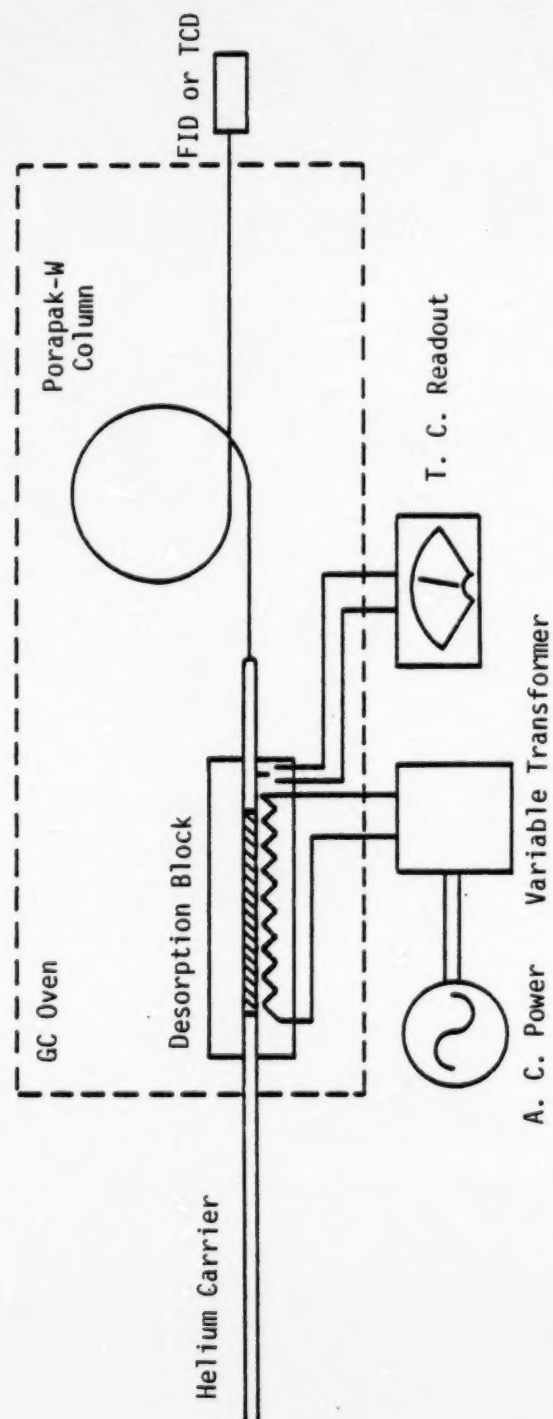
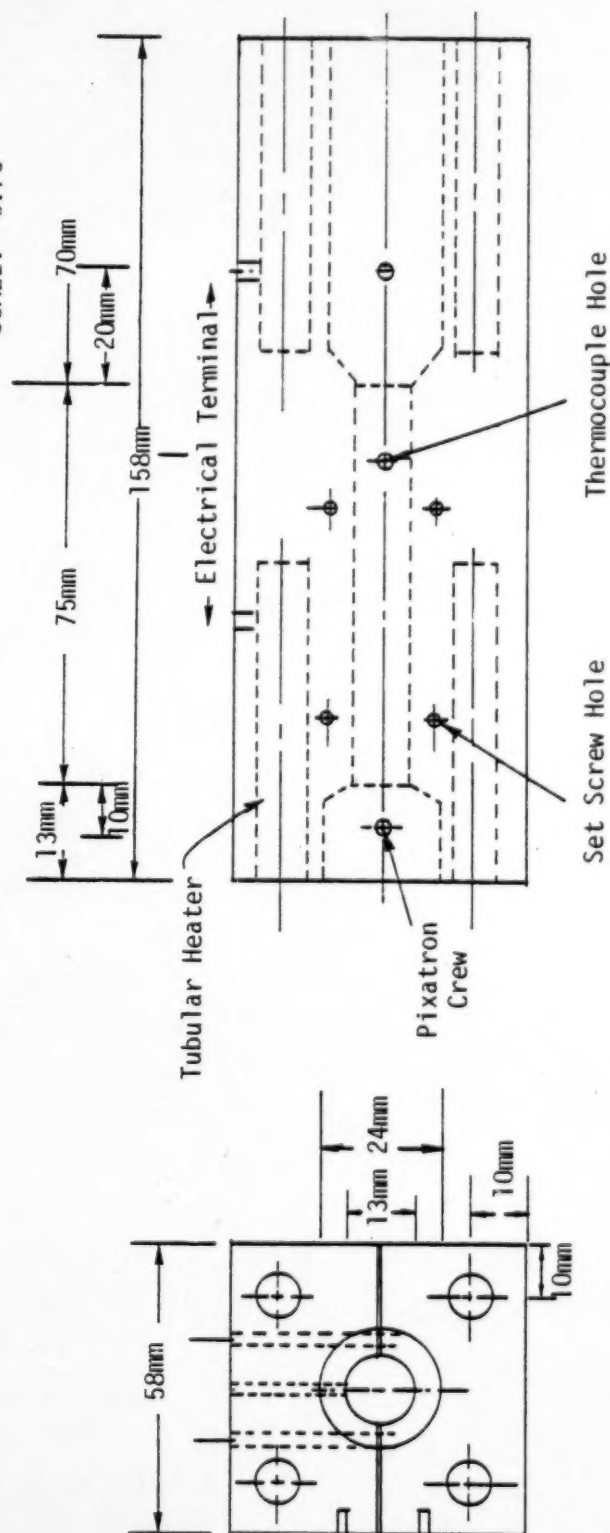


Figure B-2. Desorption and analysis equipment.

SCALE: 0.75



FRONT VIEW

TOP VIEW

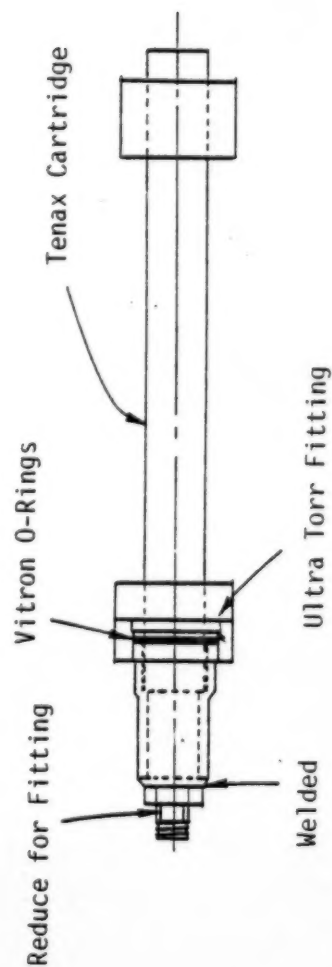


Figure B-3. Cartridge and cartridge heater detail.

Test compound calibration was performed by three independent procedures. This was necessary to determine the inherent scatter and reproducibility of the measurement technique, and to locate any systematic errors that appeared in any of the calibration tests. The three techniques were 1) direct syringe injection of test compound onto the GC column; 2) syringe injection of liquid test compound into a Tenax cartridge, followed by routine desorption and analysis; and 3) preparation of known standards in a dilution tank, followed by routine Tenax sampling and analysis of the tank contents.

Direct Column Injection: Liquid samples were withdrawn with a calibrated microliter syringe and directly injected onto the column through the injection septa. Chromatograph conditions were identical to the nominal operation procedure except:

1. The Tenax cartridge desorber was not a part of the system.
2. Rather than follow the prescribed oven temperature programming, an isothermal temperature of 120°C was used (except for chlorobenzene where 180°C was used). The isothermal temperatures increased the speed at which calibrations were performed. The programming is necessary during normal sampling to separate light hydrocarbons from the earliest test compound peaks. Because of the linearity of the FID amplifier, the change in temperature programming does not affect the calibration.

Table B-1 lists the FID mass sensitivity for the various compounds tested, relative to methane.

Syringe Injection Onto Tenax: Liquid test compound samples were directly injected onto packed Tenax cartridges. These were subsequently desorbed and analyzed. The results in the present study were used as an initial, qualitative test for breakthrough volume. After injection, helium was drawn through the cartridge. For some tests a second cartridge was placed behind the first. Breakthrough was selected by the appearance of test compound on the second cartridge and, simultaneously, by the loss of response from the analysis of the first cartridge.

TABLE B-1. MASS SENSITIVITY RELATIVE TO METHANE FOR THE FID

| Compound           | Relative Sensi-<br>tivity | Compound            | Relative Sensi-<br>tivity |
|--------------------|---------------------------|---------------------|---------------------------|
| Acrolein           | 0.54                      | Ethyl Acrylate      | 0.59                      |
| Phenol             | 1.22                      | Hexachlorobenzene   | 0.0                       |
| Benzene            | 1.23                      | Toluene             | 1.09                      |
| Carbon Disulfide   | 0.0                       | Vinyl Chloride      | 0.69                      |
| Acrylonitrile      | 0.59                      | Methyl Ethyl Ketone | 0.68                      |
| 1,2-Dichloroethane | 0.32                      | Chlorobenzene       | 0.77                      |
| Chloroform         | 0.09                      |                     |                           |

Dilution Tank: Dilute samples were prepared by evacuating an 11-liter glass tank and injecting a known amount of sample into the tank as the tank was rapidly repressurized. After repressurization the tank was allowed to equilibrate and the tank pressure and temperature were noted for calculation of the correct dilution factor. A portion of the tank contents are pumped through the Tenax sampling system. The remainder of the calibration test is identical to the normal sampling and analytical procedure.

#### B.5 Calibrations

Figures B-4 through B-7 show the calibration plots for benzene, chlorobenzene, chloroform, and acrylonitrile. These are plotted as microliters liquid vs. integrator peak area. The two plots shown on each graph correspond to the direct injection calibration and the Tenax calibration. The close agreement between the two curves for all compounds indicates that breakthrough volume was not exceeded for these compounds. This was confirmed by the absence of measurable test compound on the second cartridge.

#### B.6 Optimization

The Tenax calibration apparatus was used to optimize the response with respect to total sample flow rate. In addition, the breakthrough volume for each of the test compounds was determined.

Flow Rate Optimization: Previous work with Tenax has indicated that maximum breakthrough volume is a function of sample flow rate. Either excessive or too-low flow can result in breakthrough. The experimental sample flow rate was selected for the present study by varying sample flow for a gas containing 45.8 ppm benzene and determining the fraction captured. The results are shown in Figure B-8 and indicate that 0.19 to 0.28 liters/min. sample flow optimizes capture.

Volumetric Breakthrough: The breakthrough of each compound was measured for the standard 0.23 liters/min. flow rate and 10-min. sampling period, and for 3.7 liters total volume. These results are shown in Table B-2 and indicate that only acrylonitrile and chloroform show significant breakthrough at 3.7 liters, and at the normal 2.3-liter volume the maximum breakthrough for acrylonitrile was an insignificant 0.4 percent.

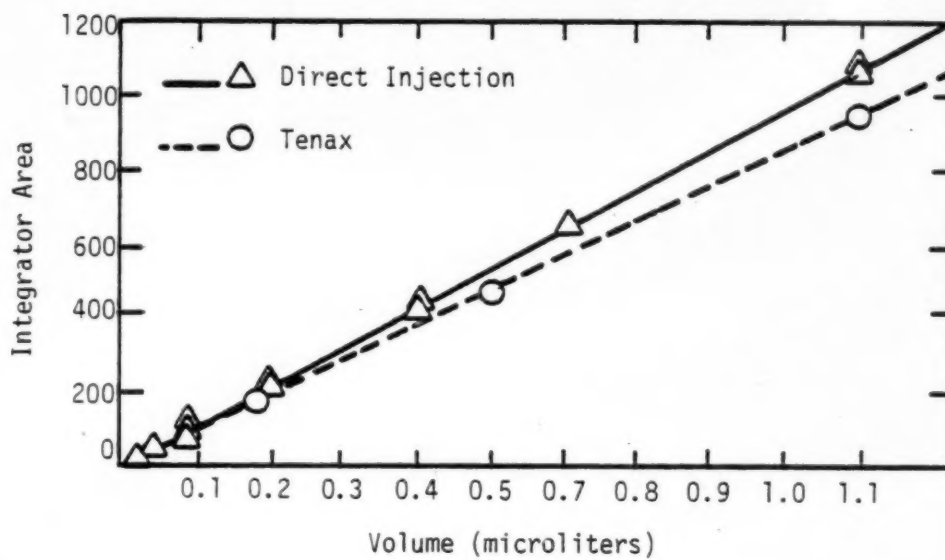


Figure B-4. Calibration curves for 1,2-dichloroethane.

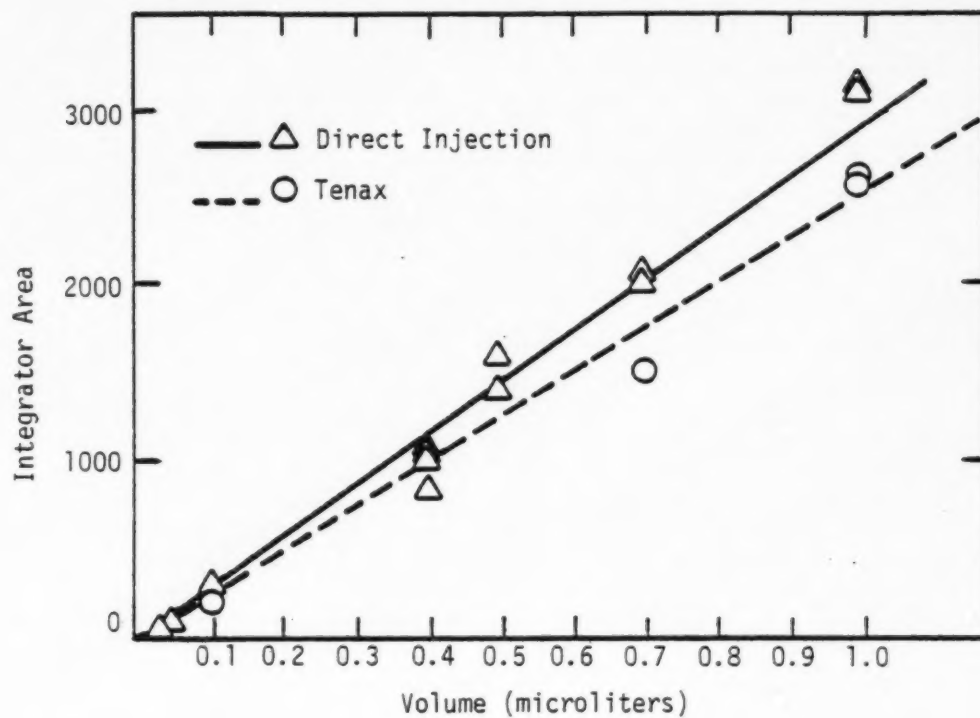


Figure B-5. Calibration curves for benzene.

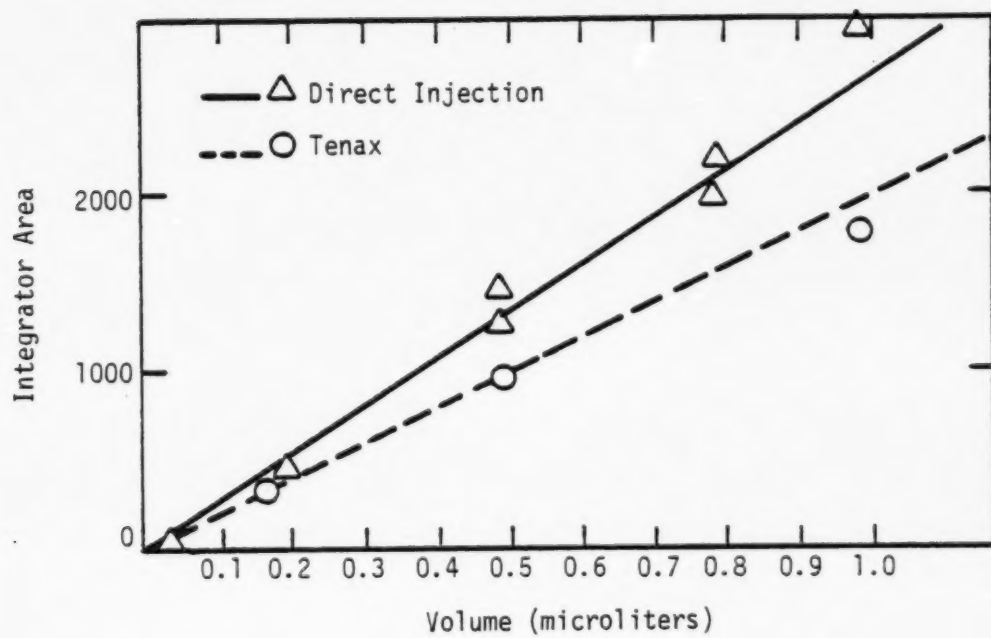


Figure B-6. Calibration curves for chlorobenzene.

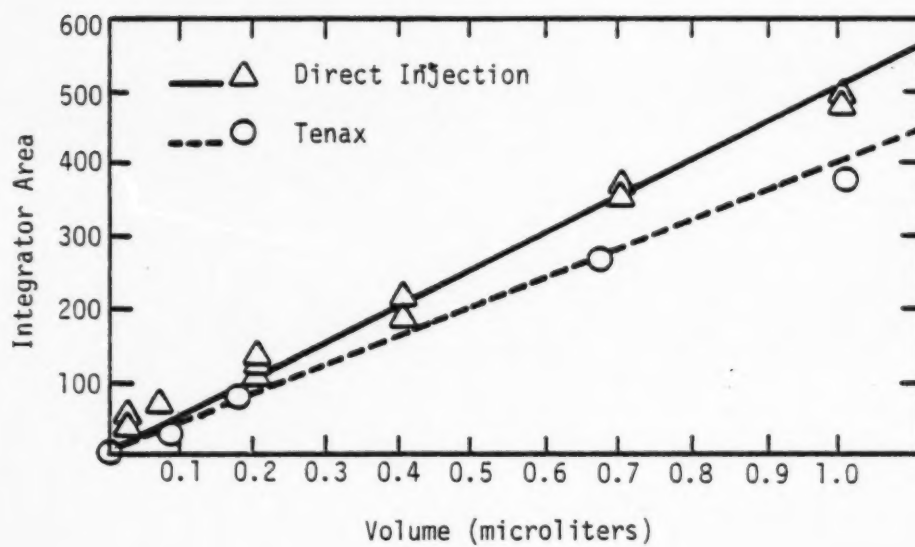


Figure B-7. Calibration curves for chloroform.

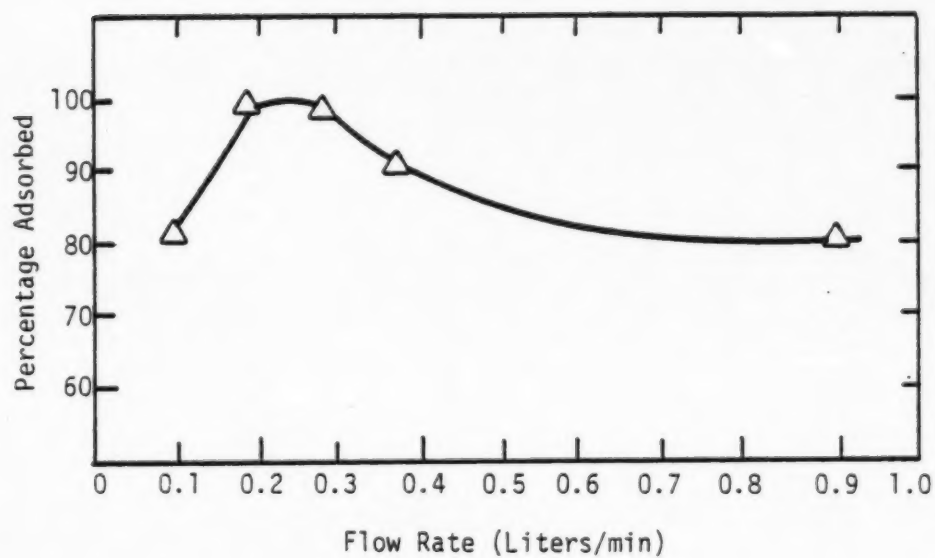


Figure B-8. Adsorption efficiency of a 45.8 ppm benzene stream onto Tenax as a function of flow rate.

TABLE B-2. VOLUMETRIC BREAKTHROUGH MEASUREMENT

| Compound      | Percent Breakthrough |                |
|---------------|----------------------|----------------|
|               | V = 3.7 Liters       | V = 2.3 Liters |
| Acrylonitrile | 17.4                 | 0.4            |
| Benzene       | 0.05                 | 0.0            |
| Chloroform    | 3.40                 | 0.06           |
| Chlorobenzene | 0.0                  | 0.0            |

Flow Rate = 0.23 liters/min.

Concentration = 100 ppm

Sample Storage: Each GC analysis required about 1.5 hours. Thus, a backlog of unanalyzed samples occasionally accumulated. In no case was a sample held longer than 24 hours before analysis. However, a series of tests were performed to determine if 24 hours was a safe period for storage. A standard gas was prepared and adsorbed onto two cartridges in parallel. The first was analyzed immediately and the second was stored under nominal storage conditions for 24 hours and analyzed. The results, shown in Table B-3, indicate that no significant loss of test compound occurred. The scatter between the two analyses is typical of the measurement technique.

TABLE B-3. SAMPLE STORAGE STABILITY

| Compound      | Analysis           |                         |
|---------------|--------------------|-------------------------|
|               | Immediate<br>(ppm) | After 24<br>Hours (ppm) |
| Acrylonitrile | 16.7               | 18.2                    |
| Chloroform    | 16.2               | 14.5                    |
| Chlorobenzene | 8.77               | 9.5                     |